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Mercury Maps

A Quantitative Spatial Link Between Air Deposition and Fish Tissue

Peer Reviewed Final Report

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Executive Summary

Mercury Maps is a tool that relates changes in mercury air deposition rates to changes in mercury fish tissue concentrations, on a national scale. The tool utilizes a reduced form of accepted mercury fate and transport models applied to watersheds in which air deposition is the sole significant source.

The Mercury Maps model states that for long-term steady state conditions, reductions in fish tissue concentrations are expected to track linearly with reductions in air deposition watershed loads. The model utilized in this project is a reduced form of the IEM-2M and MCM models used in the Mercury Study Report to Congress (MSRC) (US EPA, 1997b), whereby the equations of these models are reduced to steady state and consolidated into a single equation relating the ratio of current/future air deposition rates to current/future fish tissue concentrations.

Mercury Maps is designed to work only with watersheds in which air deposition is the sole significant source of mercury. A key step in the project then is to identify, and eliminate from the analysis, watersheds in which mercury sources other than air deposition, such as gold mines and chlor-alkali facilities, are present and contribute loads that are significant relative to the air deposition load to that watershed.

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Introduction

The goal of the Mercury Maps project is to establish a tool to quantitatively evaluate the potential impact of air mercury emission reduction rules on fish tissue mercury concentrations, nationwide. Specifically, this project is proposed as a method to help evaluate the benefits of technology based air emission reduction standards, and/or to be used to evaluate and/or design a risk-based air emission reduction rule for mercury. In addition, another potential use of Mercury Maps is in performing a regional or national TMDL analysis. By relating reductions in air deposition rates to reductions in fish tissue concentrations, by watershed, this project is one component of an overall emission reduction benefits analysis. Estimates of percent air deposition reductions, by watershed, would be needed and presumably generated from a regional air deposition model, to relate air emission reductions to watershed air deposition reductions.

Method Overview

Previous modeling efforts in the MSRC (US EPA, 1997b) described the fate and transport of mercury in the watershed and aquatic ecosystem in great detail. The IEM-2M watershed model and the MCM aquatic food chain model coalesced a considerable amount of scientific studies into unified pictures of the fate and transport of mercury in the environment. The MSRC modeling studies represent the scientific understanding of the fate and transport of this complex pollutant. This project builds on that considerable effort, and relies on the validation of those models, in order to identify the minimum number of steps, or calculations, necessary to translate air deposition rates to fish tissue concentrations as the environment approaches a steady state or dynamic equilibrium in response to load reductions. The Mercury Maps model states that a ratio reduction in air deposition watershed loads will produce an equivalent ratio reduction in average fish tissue concentration in that watershed, at steady state.

To implement the model, a national data set of mercury fish tissue data were averaged across USGS HUC-8 watersheds (Figure 1). To demonstrate the ratio reduction approach, the average concentration was divided by the new methylmercury criterion, which is expressed as a concentration in fish tissue (0.3 ppm). The watersheds with potentially significant mine sources were eliminated based on the presence of gold and mercury mines in the USGS Database for Significant Deposits and the MAS/MILS databases, respectively, and the presence of mercury cell chlor-alkali facilities. In addition, watersheds in which the total estimated mercury discharge rates from Publicly Owned Treatment Works (POTWs) and pulp and paper mills, in each watershed exceeds 5% of a typical low level air deposition watershed load (10 ug/m^2/yr) as delivered to waterbodies, were eliminated from the analysis.

Results of the model implementation are presented in Figure 2. Together with air deposition model output for both baseline and control scenario average watershed loads, this project methodology could be used to relate proposed emission control scenarios with expected long term impacts on fish tissue.

Model Development

Steady State Formulation of the Mercury Cycling Model (MCM)
Hudson, et al, 1994 details the Steady State equations of the MCM. In this paper, they include the equations for both mass balance and steady state concentrations for divalent mercury, methylmercury, and elemental mercury. They also include steady state versions of the equations used in the MCM to describe the following processes: total inputs of mercury to a lake; reduction of Hg^{2+} to Hg^0; methylation of Hg^{2+} in the water column and surficial sediments; scavenging and sediment burial; out-seepage of dissolved species; demethylation in water column; and the volatilization loss of Hg from a lake.

The mass balance equations state that the sum of total inputs, reduction, methylation, scavenging/sediment burial, demethylation, volatilization loss, and out seepage (as relevant for each of the three species) must sum to zero.

The process equations, in words, state:
- Total inputs of mercury to a lake are a function of air deposition and in-seepage, and are independent of in lake concentrations;
- Mass rate of reduction of Hg^{2+} to Hg^0 is proportional to dissolved Hg^{2+} concentration;
- Mass rate of methylation of Hg^{2+} in column and surficial sediments is proportional to dissolved Hg^{2+} concentration;
- Mass rate of scavenging and sediment burial is proportional to particulate concentrations (by species);
- Mass rate of out seepage of each dissolved species is proportional to its dissolved concentration;
- Mass rate of demethylation in the water column is proportional to the dissolved methylmercury concentration;
- Mass rate of volatilization loss of Hg from a lake is proportional to concentration of that species;

The equilibrium concentration equations can be reconstructed by inserting the mass rate process equations into the mass balance equations, and solving for species concentration. Each of the resulting dissolved mercury species steady state concentration equations shows a linear relationship between concentration of the affected species and deposition rate.

The MCM describes fish methylmercury bioaccumulation as a linear function of dissolved methylmercury concentration, i.e. the standard BAF equation. Hudson, et al, 1994 also show how they obtained the best correlation with observed data ($r^2 = 0.96$) by taking into account "speciation-independent influences of limnological parameters", in particular pH and calcium concentration, while still retaining the linear relationship between dissolved methylmercury concentration and fish tissue levels.

While extreme events may unlock mercury from environmental pools, this is part of an expected

uneven response over time to reduced mercury loadings to watersheds and waterbodies. Also referred to as dynamic equilibrium, steady state in environmental systems means that concentrations may vary season to season or even year to year, but that long term averages are constant. While environmental media mercury concentrations are expected to trend downward, random fluctuations in meteorological and other environmental patterns will cause uneven responses.

Steady State Formulation of the IEM-2M Watershed Model

The IEM-2M watershed model, used in the MSRC (U.S. EPA, 1997b), describes the impact of a steady state air deposition load on watersheds and waterbodies. Specifically, it tracks concentrations of three mercury species in soil, soil pore water, and soil pore gas, as the watershed is subject to air deposition, runoff, volatilization, and the interplay between the three mercury species. IEM-2M tracks divalent, methyl-, and elemental mercury through methylation, demethylation, reduction, oxidation, and mer demethylation (conversion of methylmercury to elemental mercury).

Described in the MSRC (section 4.4, US EPA, 1997b), reaction rate constants for IEM-2M are all independent of concentration. The mass balance equations for each species, i.e. of the form:

$$V_s \cdot \frac{dC_{si}}{dt} = \ldots$$

where:

V_s = volume of watershed soil, and
C_{si} = concentration of species i in watershed soil

When set to zero, the equations of the above form can be solved simultaneously to demonstrate that each species is a linear function of air deposition.

Additionally, the MSRC describes a parameter sensitivity analysis on the IEM-2M model (p. 6-14, in Table 6-12, US EPA, 1997b). Sensitivity is expressed as the relative change in total water column mercury concentration divided by the relative change in the model parameter, in percent. The above referenced table shows soil concentration sensitivity of +100% and -100% for positive and negative changes, respectively, in the air deposition rate input parameter. That is, given a decrease in air deposition loading rate, the IEM-2M model shows the same decrease in total soil mercury concentration. The same result is shown for total water column mercury concentration (Table 6-13, US EPA, 1997b), and predatory fish mercury concentration (Table 6-14, US EPA, 1997b).

Mercury Maps Model

Building on the analysis of the steady state formulation of the MCM and IEM-2M model equations, presented above, a simple reduced-form model is derived in order to relate percent reductions in air deposition load to percent reductions in fish tissue concentration, at steady state.

The model is derived starting with the standard, steady state bioaccumulation equation:

$$C_{fish_{t1}} = BAF \cdot C_{water_{t1}} \qquad (1)$$

where:

- C_{fish_t1} and C_{water_t1} are methylmercury contaminant levels in fish and water at time t1, respectively;
- BAF is the site specific bioaccumulation factor, which is constant for a given age/length and species of fish in a specific waterbody.

For a future time, t2, when mercury contaminant levels have changed, but all other water quality parameters remain the same, the equation is rewritten:

$$C_{fish_{t2}} = BAF \cdot C_{water_{t2}} \qquad (2)$$

where:

- C_{water_t2} is the methylmercury contaminant level in water at time t2;
- C_{fish_t2} is methylmercury contaminant levels in fish of the same age/length and species as in C_{fish_t1}

Combining equations 1 and 2:

$$\frac{C_{fish_{t1}}}{C_{fish_{t2}}} = \frac{C_{water_{t1}}}{C_{water_{t2}}} \qquad (3)$$

That is, for the same age/length and species of fish in the same waterbody, the ratio of fish concentrations and the ratio of water column concentrations at different times are equivalent. Also of note is that the equation is independent of BAF, and thus can be applied from waterbody to waterbody independent of the tremendous variability in mercury BAF, associated with inter-waterbody variability in water quality parameters. Given that methylmercury water column concentrations are proportional to mercury air deposition load to a watershed, as demonstrated from the review of the IEM-2M model, equation 3 can be rewritten:

$$\frac{C_{fish_{t2}}}{C_{fish_{t1}}} = \frac{L_{Air_{t2}}}{L_{Air_{t1}}} \qquad (4)$$

where:

- L_{Air_t1} and L_{Air_t2} are the air deposition mercury loads to a waterbody at time t1 and t2, respectively

That is, mercury fish concentrations will be reduced from current levels in proportion to load reductions for the watershed. For waterbodies in which air deposition is the sole significant source, fish tissue mercury concentration reductions will be directly proportional to air deposition load reductions.

In cases where air deposition is not the sole significant source, the equation describing fish tissue fractional reduction would need to be modified as follows:

$$\frac{C_{fish_{t2}}}{C_{fish_{t1}}} = \frac{\left(L_{Air_{t2}} + L_{Other}\right)}{\left(L_{Air_{t1}} + L_{Other}\right)} \qquad (5)$$

where:

- L_{Other} = non air deposition load of mercury to waterbody

and which reduces to the simple proportional reduction, when $L_{Other} = 0$.

For the above equation, it can be shown that:

$$\frac{C_{fish_{t2}}}{C_{fish_{t1}}} = \frac{L_{Air_{t1}}}{\left(L_{Air_{t1}} + L_{Other}\right)} \cdot \frac{L_{Air_{t2}}}{L_{Air_{t1}}} + \frac{L_{Other}}{\left(L_{Air_{t1}} + L_{Other}\right)} \qquad (6)$$

which is of the form Y = mX + b
where:

Y = fractional reduction in fish tissue concentration;
X = fractional reduction in air deposition load;
m = slope; and
b = y-intercept.

It can be shown that, for equation 6, m + b = 1. As well, the intercept (b) is just the *other load* as a fraction of total load. In the case of the Everglades mercury TMDL Pilot Project, m = 0.94, while b = 0.06. That is, 6% of the total load is non-air-deposition load.

The method employed in this project, then is to eliminate from the analysis those watersheds where sources other than air deposition are significant, thus keeping b close to zero, and m close to one, reducing errors in using the direct proportion methodology (i.e. Y = X).

Taking into account *other* loads, in other than a screening level manner, is infeasible due to large uncertainties in estimating the absolute magnitude of these sources. A more detailed analysis, of individual watersheds, in these cases, is more appropriate. Screening out of watersheds with significant or potentially significant sources allows one to proceed with much greater certainty and credibility, though with a bias towards underestimating overall reductions. Equation 6 could be used to illustrate how excursions from the simple proportional reduction model, caused by the presence of *other* sources, could influence the accuracy of Mercury Map predictions. Given that watersheds in which all potentially significant non-air-deposition sources (e.g. point sources and historic mining activities) are eliminated from the analysis, these prediction errors are expected to be quite small.

While the more complex model, presented above, would allow other significant sources, to be included in the analysis, the quality of data characterizing loads from these sources is currently insufficient for use in other than a screening level approach. In this project, loads from POTWs and pulp and paper mills are simply estimates based on the product of facility flow rates and average measured mercury effluent concentrations. There was insufficient data to use a similar screening level approach for mercury cell chlor-alkali facilities and estimating loads from abandoned mines would likely require numerous high quality samples at each site. This lack of data quality was a key determinant in selecting an approach that included screening out watersheds with significant or potentially significant non-air-deposition sources. While a national statistical sampling of all permitted discharge facilities, by industry, would provide an adequate base of information to improve on this approach, no such comprehensive data set as of yet exists. In addition, it would be extremely difficult and resource intensive to attain a sufficiently precise nationwide data set on mercury loads from other nonpoint sources such as abandoned mines and bedrock erosion.

Model Uncertainty

Comparison with Detailed Study

The Everglades Pilot Project Mercury TMDL (USEPA, 2000a), determined the relationship between atmospheric Hg(II) deposition and long-term fish tissue mercury concentrations, in Everglades Site WCA 3A-15. To determine the relationship, the researchers first calibrated the E-MCM to the WCA 3A-15 site and ran the model for 100 years to achieve an approximate steady state response to the current air deposition loading rate. They compared these long-term predicted results against current measured water, sediment, and fish concentrations and found an acceptable match. They then reduced the mercury deposition load, as well as watershed mercury inflows, and ran the model for an additional 100 years; performing this process separately for 25%, 50%, 75%, and 85% reductions in overall loads. In plotting the results of the above analysis, the researchers found the relationship between fish mercury concentration and mercury air deposition rate to be linear, and to fit the equation: $Y = 0.9408X + 0.0611$, where Y = the fraction of current fish concentration; and X = fraction of current air deposition load (wet and dry). By comparison, the Mercury Maps model simply states $Y = X$ (i.e. slope =1, and intercept = 0). The reasons for the discrepancy between the two models, as well as the effect on predictive accuracy of the Mercury Maps model, in this case, are discussed below.

The researchers note the reason for the slope and intercept, of the fitted equation, not being equal to one and zero, respectively, is that even after the initial 100 year simulation, deep sediment concentrations had not yet reached a steady state response to current loading. The sediment concentrations are elevated with respect to true steady state, and thus represent an additional load beyond the reduced air deposition load. The researchers also state that were the simulations carried out for much longer periods (as long as thousands of years), predicted concentrations would approach a direct proportional response (i.e. $Y = X$).

The E-MCM model result, being not quite directly proportional, can be shown to have a quantifiable effect on the predictive accuracy of the Mercury Maps model, were it also applied to the Everglades WCA 3A-15 site. For a 50% reduction in air deposition load, the Everglades Hg TMDL application would predict a 47% reduction in fish concentrations, to Mercury Maps' 50% reduction. Higher proportional reductions result in larger prediction errors, e.g. a 90% air deposition load reduction causing a 84% fish tissue reduction in E-MCM, versus a 90% reduction in Mercury Maps.

In conclusion, sediment concentrations may, in some instances like the Everglades WCA 3A-15 site, be elevated with respect to current air deposition loads. These elevated concentrations, unaccounted for in Mercury Maps, act as an additional source and, where significant, will cause Mercury Maps to over-predict reductions in fish tissue concentrations. In the case of the Everglades site WCA 3A-15, the quantified over-prediction is relatively small, on the order of up to five percent at high air deposition rate reductions. In addition, it can be reasonably expected that similar situations exist in other watersheds throughout the U.S., where historic atmospheric mercury deposition and continued mercury accumulation in sediments may cause current

sediment concentrations to be elevated with respect to current deposition levels, but that these elevated levels will cause fish concentrations to depart only slightly from the direct proportional reduction used in Mercury Maps. This small difference is likely reasonable for the purposes of benefits assessments.

Linearity Assumption

The ES&T article (DiPasquale, et al, 2000) found that demethylation rates increased with increased methylmercury concentration, in waterbodies with extreme mercury contamination, caused by historic mining practices. While this study does appear to provide real evidence of a nonlinear process with respect to mercury concentration, it is not clear whether net methylmercury bioaccumulation in fish is expected to be a nonlinear function of mercury concentration as a result. However, were nonlinear demethylation rates to affect net bioaccumulation in this way (i.e. to cause fish tissue concentration reductions to slow with decreased load) the proportional reduction approach in Mercury Maps would then overpredict reductions in fish tissue. That is, the potential implication of DiPasquale, et al, 2000 is that more dramatic deposition reductions, than those derived in the current formulation of Mercury Maps, would be required in order to achieve the methylmercury criterion in all watersheds. Conversely, for a given technological standard based emission reduction, the estimated benefits would be reduced.

Finally, it should be noted that any potential for non-linearity in the selected air deposition model should not be confused with the potential for non-linearity in watershed fate and transport. The air deposition model need not be linear with respect to source loadings to the atmosphere in order to be used in conjunction with Mercury Maps.

Use of Watershed Screening Method

It should be noted, however, that for the use of Mercury Maps in an emission reduction benefits analysis, the effect of using the watershed elimination method is to under-predict the overall benefits. The extent of this under-prediction can be bounded on the upper end as the percentage of all watersheds that are eliminated (i.e. if 20% of all watersheds are eliminated, the under prediction is, at a maximum, 20%). It should also be noted that this expected under-prediction should be within the realm of uncertainty brought in by other aspects of a benefits assessment. This approach buys a higher degree of certainty at the expense of a potentially higher benefits calculation.

Other Source Categories

Below, is a discussion on sources potentially not taken into account by this project, as well as further explanation of the reasoning behind eliminating known or likely significant point sources from the analysis. Based on the studies summarized briefly below, it appears unlikely that background sources contribute a significant fraction of the current load. Also, the error likely to

have been introduced, by not taking into account the effect of background load on predicted response, is small relative to the prediction.

A number of studies have looked at the potential relationship between mercury concentrations in soil and runoff, as well as soil/bedrock erosion as a potential mercury source. St. Louis, et al, 1996 estimated, based on comparisons with erosion rates of other minerals, that mercury weathering rates could range from 0.4% to 6% of total mercury inputs to the watershed. They deemed this amount insignificant for the purposes of the mass balance in their study. Finally, Aastrup, et al, 1991 quantified mercury accumulation and transport in a number of soil layers in a watershed, as fractions of total mercury deposited. By the use of a mass balance they demonstrated that the content and fluxes of mercury, in interflow and groundwater flow, is accounted for via the percolation of atmospherically deposited mercury through the soil. In addition, while weathering and dissolution of mercury from bedrock may be significant in some areas, these areas would likely be associated with mercury mining locations, and would be screened from the analysis on that basis.

Emissions Inventory Period and Watershed Lag Time

Mercury air emission rates have decreased recently due to a contraction of the medical waste incinerator industry in response to emission regulations, as well as recently due to new MACT rules for Medical Waste Incinerators and Municipal Waste Combustors (SAI, 1998)
Since there is a time lag from emission to accumulation in fish, the time period over which fish tissue concentrations are measured represents an earlier period of emissions. A plot of fish sample records count by year is shown in figure 3, with a distinct peak in 1993 and the bulk of samples from 1990-1995. Given that emission rates have decreased significantly over the last 1-2 decades, and lag time may be as long as 1-2 decades, fish concentrations may be slightly elevated with respect to ‘95-‘96 emission levels (recent air deposition modeling studies have used a ‘95-‘96 emissions inventory baseline year).

If ‘90-‘95 fish tissue is elevated with respect to expected steady state fish tissue concentration values for the ‘95-'96 emission levels, predicted future fish concentrations will be higher than would ultimately occur. In terms of a benefits assessment, then, this model and data set is expected to systematically under-predict reductions in ultimate fish tissue concentrations resulting from an emissions rule, as compared against ‘95-‘96 emission levels. Similarly, a risk-based emission reduction rule, designed to achieve criterion levels, using this method, would be expected to produce emission reductions beyond the minimum necessary to achieve the criterion. The uncertainty caused by the effect of lag time and a gradual reduction in mercury emissions over the last 1-2 decades, is a non-quantified margin of safety. This uncertainty could be reduced and/or quantified by a more detailed analysis of trends in U.S. mercury emissions and studies of lag times. Other data quality issues and limitations, by data layer, are detailed in the Appendix.

In addition, while the accuracy of predictions of fish tissue reductions in Mercury Maps will be a direct reflection of the accuracy of the air deposition model in predicting relative rates of air

deposition of mercury to watersheds, this project is not dependent on the use of any particular deposition model. Rather, this project is intended to be coupled with the air deposition model thought best able to predict percent reductions in mercury deposition on a national scale.

Model Implementation

The first step in implementation of the Mercury Maps model, was to average the fish tissue data by watershed boundary. As the exposure endpoint of concern is chronic consumption of contaminated fish, an individual is expected to be exposed, over the long term, to average concentrations. The National Listing of Fish and Wildlife Advisories (NLFWA) fish tissue database (described in more detail in the appendix) was processed in ArcView according to the following steps:

- select only samples listed as fillets (inlcuding both *skin on* and *skin off*);
- spatially merge fish tissue sampling locations with watershed boundary data;
- run summarize function to determine the average fish concentration by watershed;
- create a new field and calculate the ratio of the criteria to the average concentration to show the percent reduction in total mercury load required to meet the criteria.

Since these fish tissue data are used by States in making decisions on whether to post fishing advisories, the fish sampled may not be truly representative of the true population average across the HUC. These samples are in fact generally based on areas that are most heavily fished (*angling pressure*) and/or those that are suspected of having higher than average potential to be polluted (AFS, 2000). That is, the average concentration may be biased higher with respect to the true average, but would be expected to be more reflective of the average concentrations in consumed freshwater fish. While a statistical sampling would produce a less biased average concentration, the goal of protecting human health is better served by sampling with a bias towards areas, that with sound scientific reasons, are suspected of having higher than average concentrations, or that account for a disproportionate amount of fish caught and consumed. The manner in which fish tissue is sampled is a decision made by the state agency. Additional analyses on the fish tissue data are included in the Appendix. It should be noted that the median number of samples per HUC is 9 (mean is 24), which is a reasonable statistical sample on which to base a mean.

A statistical analysis of the different sample types was performed. It was found that there were large differences between fillet and whole fish concentrations (0.40 ppm vs. 0.18 ppm, respectively), as well as between fillets with *skin off* versus fillets with *skin on* (0.40 ppm vs. 0.31 ppm, respectively). It was also shown that these differences in concentrations may be due in large part to differences in species sampled. Whole fish samples are more frequently trophic level 3 fish, while having skin on or off appears to be a function of how a particular fish species is typically consumed (see Appendix for details). Based on this analysis, and because for the purposes of benefits assessment, TMDLs, and risk-based emission control rules, the consumed concentration is most relevant. Whole fish samples, then, are eliminated from the analysis, and

all fillets (skin on and skin off) are included. All unknown and unspecified sample types are eliminated from the analysis.

A preliminary analysis of the effect of using a finer resolution watershed coverage was performed. The HUC-11 watershed coverage, readily available for the Chesapeake Bay watershed, was added to the project, and fish tissue data were aggregated to that level of resolution. The resulting map of the average fish tissue concentration relative to the methylmercury criterion showed a few local maxima that had been smoothed out at the higher resolution HUC8 watershed scale, as is to be expected. An analysis, presented in the Appendix (fish tissue database section), however, shows that the median number of samples in the HUC11 watersheds is 3, while the median in HUC8 watersheds is 9. That is, while the fish tissue database is substantial, it is not large enough to justify averaging across watersheds smaller than the HUC8 level. Analyses at smaller levels is justified on a case by case basis, and may be appropriate in a sentinel-watershed approach associated with a risk-based air emission reduction rule analysis, or a TMDL.

In the next step in the model implementation, watersheds influenced by mercury loads from historic gold and mercury mines, or by current chlor-alkali facilities, were eliminated from the analysis.

Mercury Mines:
Plouffe, et al found elevated mercury concentrations in soils surrounding mercury mines, at distances of up to 20 km to 40 km. Thus, it appears reasonable to suspect mercury mines as likely sources of elevated environmental concentrations of mercury.

Gold Mines:
The MAS/MILS database included numerous locations, with gold as a commodity, that were likely insignificant sources and may have never used the mercury amalgamation process. An alternate database, the USGS Database of Significant Deposits of Gold, Silver, Copper, Lead, and Zinc in the United States was used instead (Long, et al, 1998). This database was queried for mines that have produced more than two tons of gold. Any watershed containing one or more of these mines was screened from the analysis, on the basis of potential historical contamination of the watershed due to use of the mercury amalgamation process.

Chlor-Alkali Facilities:
The Mercury Study Report to Congress (MSRC) (EPA, 1997) notes that only a fraction of chlor-alkali facilities use the mercury cell process. MSRC lists the 14 facilities using the process at that time and notes that no new mercury cell chlor-alkali facilities are planned to be built, while a recent study (EPA, 2001) found a much lower loading rate than reported in PCS (see Appendix for details). However, because, recent data were available for only one mercury cell chlor-alkali plant, there were insufficient data to assign an average value across all plants, in a screening approach, similar to that for pulp and paper mills. Instead, the simple presence of a plant was used to screen out watersheds.

The spatial data processing steps were as follows:

- query mines databases (described in more detail in the appendix) for all mercury producing mines or mineral locations and all significant past producers of gold;
- export selected gold and mercury locations data and import back in as separate themes;
- use "select by theme" command to identify and eliminate from the analysis, all watersheds that contained at least one gold or mercury location.

In the third and final step in model implementation, watersheds with significant point source mercury discharge loads were eliminated. A number of reports have inventoried mercury discharge to water suggesting alternative methods of taking inventory of mercury discharges to surface waters. A recent study by EPA Office of Research and Development (US EPA, 2000b) examined mercury use in five major categories of type of use, and estimated mercury release to the environment by source category. The report identified four sources of mercury discharge to water with estimated total annual loads: Chlor-Alkali Production (0.1 tons/yr), Utility Coal Combustion (7 tons/yr), and Sewage Treatment and Sludge Incineration (15-30 tons/yr), and Dental Offices (7.4 tons/yr). The report used TRI data for chlor-alkali plants, an estimate of measured concentrations from cooling tower blowdown for the utility coal combustion category, and PCS data to estimate the WWTP load. Dental offices, while estimated separately in the report, would, for the most part, be incorporated in the WWTP value. The National Sediment Inventory (NSI) (U.S. EPA, 1997) compiled an inventory of point source dischargers of mercury to the waterways of the U.S. In this study, they found that the Toxics Release Inventory (TRI) showed 14 facilities discharging 271 lbs/yr while the Permit Compliance System (PCS) showed 749 facilities discharging a total of 28,592 lbs/yr, clearly indicating PCS is more comprehensive. However, because of known uncertainties in PCS data for mercury, a new methodology for screening out sources was developed.

Pulp and Paper Mills

A detailed review of a study conducted by the Maine DEP (ME DEP, 2001) found the expected loading rate for both pulp mills and paper mills to be 3.1 lb/yr. That is, the 14 pulp and paper mills in the study had an average concentration of 13 ppt, and an average flow rate of 79 MGD (see Appendix for details). By contrast, PCS data showed average loading data of 10 lb/yr for pulp mills and 40 lb/yr for paper mills (see Appendix for details). Additional data on POTW facilities from PCS, in contrast with a clean sampling and analysis study by AMSA, indicates further contamination problems with the PCS data. As a result of these efforts, discussed in detail below, it was confirmed that the PCS data is likely based on non-ultra-clean techniques. These data will not be used.

Publicly Owned Treatment Works (POTWs):

Using a study conducted by the Association of Metropolitan Sewerage Agencies (AMSA) on mercury in POTW effluent, a sensitivity analysis was performed to examine the relative loading from POTWs versus air deposition delivered to waterbodies. Nellor, 1999 cites an average mercury concentration in POTW effluents of 7.25 ppt (ng/L). This data is based on AMSA's study of 24 POTW facilities in six states, using clean sampling and analytical techniques, for

facilities with a range of flow rates from 0.65 MGD to 225 MGD. The range in mercury effluent concentrations was 0.7 ppt to 69.9 ppt, with a median value of 5.0 ppt.

For the purposes of this study, the mean value of 7 ng/L was applied to each POTW, at the PCS reported flow rate, and their cumulative load was summed (across HUCs). This loading rate is compared to a typical air deposition load of 10 ug/m2/yr, with an assumed 20% delivery to waterbodies (discussed below). If the sum of POTW mercury loads is greater than 5% of the air deposition load, as delivered to waterbodies, then the watershed is screened from the analysis. 79 watersheds were screened out solely on the basis of this procedure, all located west of the Mississippi River. Additional details on this analysis, as well as on the mercury data available in the PCS database, are available in the Appendix.

In order to compare the estimated point source mercury load data against average deposition rate, the total estimated load for all key sources is compared against mercury load, delivered to waterbodies. That is, PCS data were used to eliminate watersheds as having significant point source discharge only if the sum of PCS discharge in the watershed was greater than 5% of the typical ($10ug/m^2/yr$) deposition rate as delivered to waterbodies. See Hydrologic Cataloging Unit Boundary theme in appendix for calculations of average deposition load by watershed.

The following is a review of the literature on the percent of total atmospheric deposited mercury which is transported from watersheds to receiving waterbodies.

- Aastrup, et al, 1991 found yearly mercury transport to a lake from a forested subcatchment to be 17% of total mercury deposition.
- Lindberg, 1996 found the combination of runoff and leaching to total 3.5% of total atmospheric load of mercury to the Walker Branch watershed, TN.
- St. Louis, et al, 1996 found that for five catchments in the Experimental Lakes Area (ELA) in northwestern Ontario, export of total mercury ranged from an average of 29.5% for a basin wetland to 61.1% for a riverine wetland.
- Sherbatskoy, et al, 1998 found an export rate of 6% of total mercury from a small forested catchment in Vermont.
- Swain, et al, 1992 found for catchments to seven headwater lakes in Minnesota and Wisconsin, the proportion of atmospheric mercury transported from catchment to lake to be 26% and 22% for modern and pre-industrial times, respectively.
- Hurley, et al, 1995, found watershed total mercury transfer efficiencies, for 39 river sites in Wisconsin to range from Fall means of 0.5% to 8% (depending on watershed type) to Spring means of 29% to 90%.
- Tsiros and Ambrose, 1999 found delivery of mercury to canals in the Everglades Agricultural Area was 23% of atmospheric deposition.
- Johansson et al. (1991) reported mercury transport fluxes from several small watersheds to be about 30% of atmospheric deposition.
- Tsiros, 2001, in model simulations, found that mercury runoff flux was 2 to 3 times higher than normal during wet years, and 5 to 7 times lower than normal during dry years, and that mercury runoff flux was 18% to 61% of atmospheric deposition for wet years,

and 1% to 4% of deposition for dry years. These values correspond to runoff flux for normal years to be between 6% and 30% of deposition.

Based on a review of the above studies, it appears that a delivery ratio of 20% is a reasonable estimate of the central tendency of this value, an appropriate estimate for the purposes of this study. That is to say, on average, it's expected that only 20% of air deposited mercury reaches waterbodies on a long-term average annual rate. So, watersheds in which the sum of loads from pulp and paper mills and POTWs is greater than 5% of the nominal air deposition load to waterbodies (20% of watershed deposited mercury) are screened from the analysis.

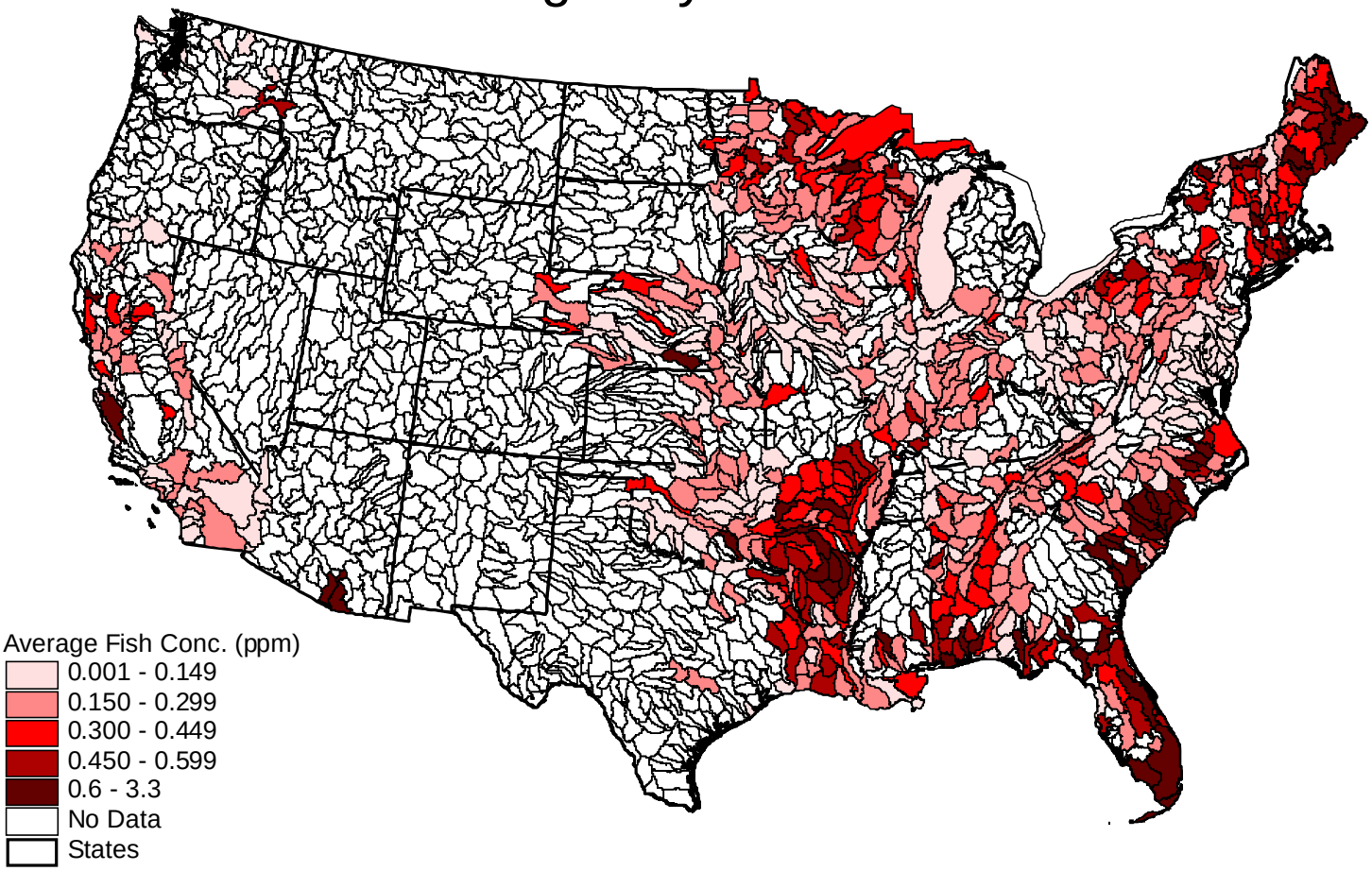
Results and Interpretation

The results of the model application are shown in Figure 2, which shows the ratio reduction in air deposition, by watershed, required to meet the new methylmercury criterion. Watersheds colored red indicate where fish concentrations exceed the criterion, while those colored green indicate watersheds in which no reductions are necessary and are unlikely to have a fish advisory. Watershed outlines with no color indicate no available fish tissue data, while those highlighted yellow are watersheds eliminated due to the presence of a significant estimated mercury load from POTWs, and/or pulp and paper mills, and/or the presence of mercury mines, gold mines, or chlor-alkali facilities. Of all the watersheds with reported fish tissue mercury concentration data, only a few in the western third of the U.S. were not eliminated from the analysis, due to the presence of mines and other sources

For an emission reduction rule benefits analysis, predicted percent reductions in air deposition rates (average by watershed) would be applied to current average fish concentrations, to predict future steady state fish concentrations at the proposed rule emission level. Predicted average concentration could then be compared against the points of departure for fish advisories to determine if an advisory would be lifted. Tissue concentration reductions could also be used to estimate incremental health benefit of reduced body burden as a result of the reductions.

In addition to the dataset-specific background information and analysis, information on how each data layer was processed is detailed in each section of the Appendix. It is recommended that future users check the calculations and datasets used to determine whether all calculations and data processing were performed correctly.

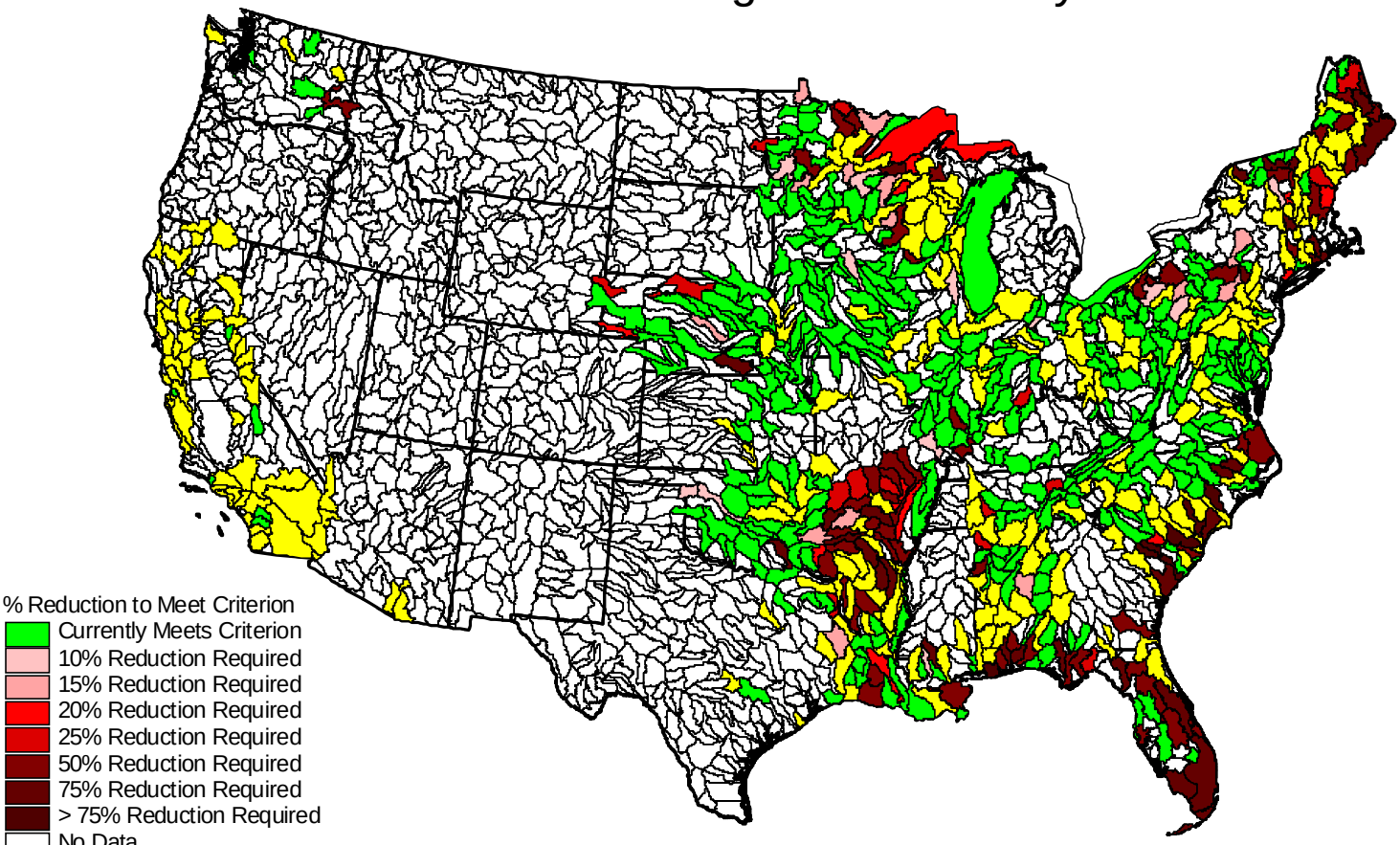
Fish Tissue Mercury Concentrations Averaged by Watershed



Note: New Criterion for mercury in fish is 0.3 ppm. Point of departure in fish advisories often in 0.15 ppm to 0.3 ppm range.
Average value based on fillet samples only. See report text for details.
Source: National Listing of Fish and Wildlife Advisories (NLFWA) Mercury Fish Tissue Database (June, 2001).

Figure 1

Percent Reduction in Air Deposition Load Necessary to Meet New Methylmercury Criterion Watersheds with No Other Significant Mercury Sources



Note: Watersheds highlighted yellow have significant non-deposition mercury sources defined as where the total estimated load from Publicly Owned Treatment Works (POTWs) and pulp and paper mills is greater than 5% of estimated waterbody delivered mercury at a typical deposition load (10 g/km2/yr), and/or where mercury cell chlor-alkali facilities, mercury mines, or significant past producer gold mines are present. Additional reductions would be required to meet most state fish advisory levels, which are often set below the methylmercury criterion. Source: National Listing of Fish and Wildlife Advisories (NLFWA) Mercury Fish Tissue Database (June, 2001). See text of report for data sources for point source dischargers and mines.

Figure 2

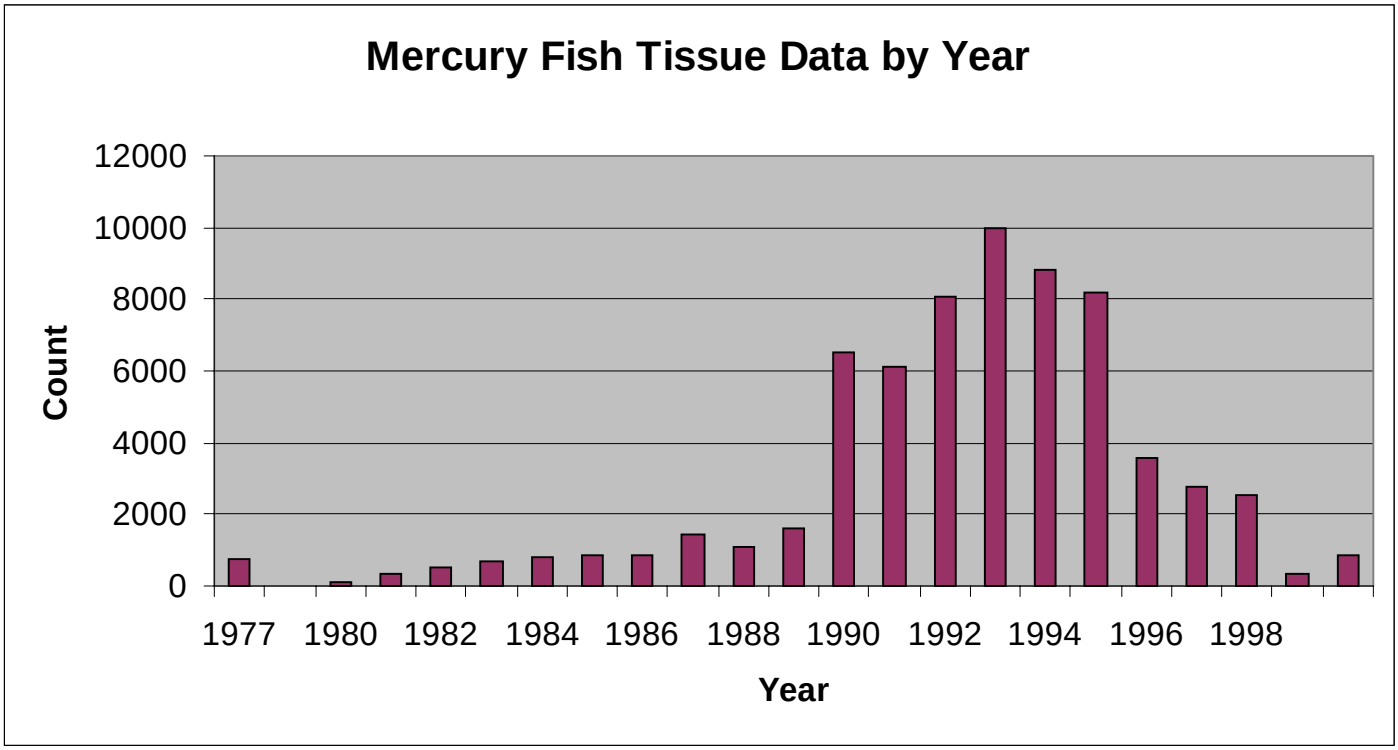


Figure 3. Counts of Fish Tissue Mercury Data Records by Year.
Source: National Listing of Fish and Wildlife Advisories (NLFWA) Fish Tissue Database (September, 2000).

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Appendix A
Mercury Fish Tissue Data Layer

Source:
National Listing of Fish and Wildlife Advisories (NLFWA) Mercury Fish Tissue Database (as of June, 2001) (US EPA, 2000c). The NLFWA database includes data from The National Survey of Mercury Concentrations in Fish 1990-1995 (Cadmus, 1997), as well as other data provided by states to the EPA Fish Advisory Program. In both cases, data were provided voluntarily by states, in response to an EPA survey. Data is currently uploaded by states directly to the fish advisory program web site.

Data Processing:
The fish tissue database was cut to include only mercury concentration results and provided as a single dbf data table. Sample records with latitude/longitude values (georeferenced samples) were added to the project using the ArcView Add Event Theme command.

Statistics:
The fish tissue database is apparently biased towards trophic level 4 fish (typically sport fish). Looking at the top ten most frequent species of georeferenced samples, 12,422 (83%) are trophic level 4 (largemouth bass, walleye, northern pike, channel catfish, yellow perch, and smallmouth bass, in descending order of frequency), while 2,608 (17%) are trophic level 3 (common carp, bluegill sunfish, white sucker, and black crappie, again in descending order of frequency).

Since methylmercury accumulates in fish muscle, rather than fat, skin, or organs, the manner in which fish samples are analyzed affects the reported concentration. Using whole fish samples will give a reduced concentration, relative to fillets, due to a dilution effect from lower concentrations in non-fillet portions of the fish. While whole fish samples are relevant for concerns over eco-system effects, whole fish sampling is not recommended for use in creating fish consumption advisories (USEPA, 2000d).

Of the 21,571 geo-referenced fish tissue samples:

- 17,826 (83%) samples were fillets,
- 1,759 (8%) were whole, and
- 1,986 (9%) were unknown/unspecified.

States in which whole fish sampling composes greater than 25% of all samples, are: GA, IN, KS, MD, ME, NE, and TX. States in which sample type is largely unknown or unspecified are MS (unknown), and TX (year sampled, unknown). About a third of samples in GA are of *unknown* sample type.

Of the fillet samples:

- 3,969 specified with Skin Off,
- 7,570 with Skin On, and
- 5,984 did not specify.

Of all 21,571 samples, only 8 indicated composite sampling, sampled at two separate locations, all done with fillets.

Of the 21,571 geo-referenced samples:

- All fillet shows average concentration of 0.40 ppm;
- All whole shows average concentration of 0.18 ppm;
- Fillet Skin Off shows an average concentration of 0.40 ppm; while
- Fillet Skin On shows average concentration of 0.31 ppm.

In order to assess whether the fish tissue data were biased toward higher trophic level fish, fish tissue samples were sorted by frequency according to species. Of the top five most frequently sampled species of georeferenced whole fish samples, 53% were trophic level 4 fish versus 46% as trophic level 3 fish. Of the five most frequently sampled species of georeferenced fillet samples, 100% were trophic level 4 fish.

Thus, the large difference in concentrations from fillet to whole fish samples is certainly due in part to the different species sampled. However, dilution from using whole fish is still expected to be significant and thus these samples will be removed from the analysis.

The top five most frequently sampled *Fillet Skin On* species were: walleye, northern pike, yellow perch, largemouth bass, and common carp, in that order. While, the top five most frequently sampled *Fillet Skin Off* species were: largemouth bass, channel catfish, white crappie, flathead catfish, and blue catfish, in that order. Based on this listing, it is clear that skin removal is species specific, and likely due to how the fish is commonly consumed. While leaving skin on dilutes the tissue concentration, it appears the choice to remove or retain the skin is representative of how that fish is expected to be consumed, and thus most representative of the concentration consumed. That is, all *fillet* samples, regardless of whether skin is specified as on, off, or unspecified, will be retained in this analysis.

Sensitivity to Scale (HUC8 versus HUC11) Analysis

The HUC11 watershed coverage was obtained for the Chesapeake Bay drainage. The HUC11 coverage contained 511 HUC11 watersheds compared to 65 in the HUC8 coverage, for the same area, nearly a factor of 8 increase in resolution.

The georeferenced fish tissue data were averaged across the HUC11 watersheds, and compared against the HUC8 coverage. Of the 116 Chesapeake Bay HUC11 watersheds with fish sample data, the median number of samples is 3 (mean of 5), with a range of 1 to 101 (26% have 1 sample). Of the 850 HUC8 watersheds (across the country) with fish tissue data, the median number of samples is 9 (mean of 24), with a range of 1 to 959 (Everglades) samples (11% have 1 sample). While 9 samples should provide a relatively solid statistical measure of the average concentration in the watershed, 3 samples provides a much lower level of statistical significance. At the same time, the dramatic increase in 1 sample watersheds is even more problematic. While the HUC11 watersheds, then, show local maxima exceeding the criterion within HUC8

watersheds shown to be below that level, these high average concentrations are not likely representative.

Notes on Data Quality and Interpretation:
This database is not a statistical sampling of fish tissue across the country. Instead, it is based on sampling directed towards areas of suspected contamination or fishing pressure. In addition, some states may not report data when resultant concentrations were found to be below state fish advisory point-of-departure levels. For the above reasons, this data should not be considered a complete characterization of the spatial distribution of mercury contaminant levels in fish.

Also, since advisories may be based on multiple pollutants, reducing fish mercury levels to below advisory levels will not result in lifting the advisory in all cases. Sustained contaminant levels for other pollutants could cause the advisory to remain in place.

Appendix B
Hydrologic Cataloging Unit Boundaries Data Layer

Source:
The USGS eight digit hydrologic cataloging unit (HUC-8) boundaries data layer is provided on the BASINS 2.0 CDs (US EPA, 1998b through US EPA, 1998k) as EPA-regional coverages (in ArcView shapefile format). Meta data is available for this data layer at the BASINS web page: http://www.epa.gov/ost/basins/metadata/hydunits.htm

Data Processing:
Hydrologic cataloging unit boundary themes for each EPA Region were combined into a single data layer using the ArcView merge command. The theme was projected as Standard Albers Equal Area projection. A field representing average deposition rate was added to the theme attribute table. Values for this field were calculated as the area in square meters times the "average" total mercury deposition rate of 10 ug/m^2/yr (equivalent to 10 g/km^2/yr). 10 g/km^2/yr is a typical low mercury deposition rate for the Eastern third of the U.S. (SAI, 1998). SAI, 1998 shows deposition rates for the Eastern third of the U.S. at typically >5 g/km^2/yr and with ~95% of the area at less than 50 g/km^2/yr. The majority of the area receives deposition in the range 5 g/km^2/yr to 20 g/km^2 /yr.

Statistics:
Statistics on Area of HUC-8 Watersheds and a Calculated "Average Deposition Rate" Load

Statistic	Area (m^2)	Ave. Dep. Rate Load* (lb/yr)
Count	3203	
Mean	3.8 E^9 m^2	84
Max	5.8 E^{10} m^2	1300
Min	9.6 E^7 m^2	2.1
St. Dev.	2.6 E^9 m^2	
Sum	1.2 E^{13} m^2	264,000 (132 tons)

* - Average deposition rate based on 10 g/km2/yr

Notes on Data Quality and Interpretation:
The use of an average deposition rate in screening out watersheds with significant point source water dischargers is conservative in that urban areas typically show much higher deposition rates. Higher total mercury discharges would also be expected in more urbanized watersheds, and thus those watersheds would be more likely to be screened out unnecessarily by this approach. For a benefits analysis, modeled baseline deposition rate data, averaged by watershed, could be used to refine this screening process and thus to reduce this uncertainty. Additionally, the metadata, referenced above, discusses the origins and original processing of the HUC-8 watershed theme for delivery with BASINS 2.0.

Appendix C
Database of Significant Deposits of Gold, Silver, Copper, Lead, and Zinc in the U.S.

Source:
This database was obtained directly from the database author (Long, et al, 1998), in excel spreadsheet format.

Data Processing:
Fields in the spreadsheet, not needed in the project, were deleted, and the header rows were reduced to a single row with a short, descriptive title. The data was then exported from Excel as a tab-delimited text file, imported to ArcView as a table, added to a View as an Event Theme, converted to a shapefile, and converted to the project projection. The field containing the amount of gold in ounces, previously produced at the mine, was manipulated to remove all non-numeric characters, and converted to number format. This data was queried for mines having produced at least 64,000 ounces (2 tons) of gold. The resultant selection was converted to a shapefile, and imported to Mercury Maps as the gold_mines_sig_dep shapefile.

Notes on Data Quality and Interpretation:
The derivation and quality of data in this database is discussed in considerable detail in Long, et al, 1998.

Appendix D
Minerals Available System/ Mineral Industry Location (MAS/MILS) Data Layer

Source:
Originally from U.S. Bureau of Mines, this database is provided as EPA regional data coverages (ArcView shapefile format) on the BASINS 2.0 CDs (US EPA, 1998b through US EPA, 1998k). Meta data is available for this coverage on the BASINS web page at:
http://www.epa.gov/ost/basins/metadata/mines.htm

Data Processing:
The mines themes for each EPA Region were combined into a single data layer using the ArcView merge command and was projected to the Standard Albers Equal Area projection. Mercury locations were identified, in separate queries, by queries of "gold" and "mercury" in any of the five commodities fields ("COM1" through "COM5"). Mercury sites were exported as ArcView shapefiles and re-imported to the project as separate national themes.

Statistics:
Number of Locations by Current Status

Current Status	Mercury Locations
Devel Deposit	52
Exp Prospect	500
Intermittent Producer	-
Mineral Location	119
Other	-
Past Producer	514
Producer	27
Raw Prospect	152
Temp Shutdown	1
Unknown	385

Notes on Data Quality and Interpretation:
No attempt was made to determine actual mercury loads from individual sites, or to rank likelihood of impact based on size or type (e.g. "Past Producer" and "Raw Prospect" were treated as both having the potential to cause or contribute to elevated mercury contaminant levels in a watershed). The above method is conservative, in that it may eliminate watersheds with minimal mercury impact from mercury mines and mineral locations. Also, see metadata, referenced above.

Appendix E
Permit Compliance System Data Layer

Source:

Permit Compliance System facility location coverage and pollutant loading tables are included in BASINS 3.0 CDs (US EPA, 2001b through US EPA, 2001k). The PCS facility locations data is provided as EPA regional data layers (ArcView shape file format). Loading data tables are organized by HUC-8 watershed, with all data for all facilities and years 1990-1999. While this loading data table format is different from the version 2.0, and the data has been updated through 1999, the data content is similar to version 2.0. Additional detail on this theme and associated tables can be found in the BASINS meta data available at the BASINS web page: http://www.epa.gov/ost/basins/metadata/pcs.htm.

Data Processing:

PCS locations themes for each EPA Region were combined into a single data layer using the ArcView merge command. The theme was projected to Standard Albers Equal Area projection. Loading data tables (one per HUC-8 watershed) were placed in a single directory and processed, using an AVENUE script that queries and extracts only data for "Mercury, Total (as Hg)" (parameter 71900) or "Mercury, Total Recoverable" (parameter 71901), and places the data in a single mercury loading data table. Loading data were linked to facility location by NPDES identification number in order to identify, and separate out facilities that had loading data for 1995 or later, and were not publicly owned treatment works (POTWs) (SIC code = "4952").

Statistics:

Mercury Loads for Non-POTW PCS facilities with 1995-1999 Data.

Statistic	Mercury Load (lbs)
Count	228
Mean	14
Max	1324
Min	0.0
Var.	11669.
St. Dev.	108.0
Sum	3285

Notes on Data Quality and Interpretation:

While permits specify the use of test methods approved by the EPA, new mercury water column test procedures (that have a substantially lower detection limit than old methods) were not approved until July, 1999. Since permits would have to be reissued/modified to require use of the new method, most of the data in the 1990-1999 PCS data base is likely based on the old method. Additionally, facilities may not use clean sampling techniques unless subject to enforcement after high monitoring results. Instead of PCS mercury loading data, then, studies with a statistical sample for POTWs and pulp and paper mills were located that could be used to screen out watersheds with significant contributions from point source discharges. Each of three

PCS facility types, and associated non-PCS monitoring data sets and interpretation are discussed below, by facility type.

Pulp and Paper Mills:
A separate theme for pulp and paper mills was created from the PCS theme by selecting facilities with SIC = 2611 (Pulp mills), 2621 (Paper mills), or 2631 (Paperboard mills). The PCS database includes 488 pulp and paper mill facilities, distributed as follows:

- 160 Pulp mills
- 244 Paper mills
- 84 Paperboard mills

PCS Loading Data:
The PCS pulp and paper theme was joined with the mercury loading data table, and summarized by year. For each year from 1990 to 1999, between 4 and 14 pulp and paper facilities reported mercury loads. The average load ranged from 5 lbs/year to 228 lbs/year, with the 228 lbs/year value appearing to be an outlier (next highest value is 22 lbs/year and is associated with a facility in Ohio reporting a load of 1324 lbs, and another in NC reporting 261 lbs in 1996). For each of the mill types, the data was summarized by facility (i.e. average load over the ten year period). Of the 27 facilities, average load was 0.0 lbs/year for six of these facilities.

- Pulp mills (SIC = 2611) - average load (by year) ranged from 1.7 to 27 lbs/year, with overall mean of 9.1 lbs/yr.
- Paper mills (SIC = 2621) - average load (by year) ranged from 0.0 to 331 lbs/year, where 7 out of 10 years, average load is less than 5 lbs/year, with overall mean of 35 lbs/year.
- Paperboard mills (SIC = 2631) - average load (by year) ranged from 14 to 261 lbs/year, and overall mean of 44 lbs/year.

Maine Study (1998) Data:
The PCS pulp and paper theme was queried to identify facilities in Maine (NPDES id starting with “ME”) and with SIC codes of 2611, 2621, or 2631, resulting in 17 facilities including:

- 4 Pulp Mills (2611)
- 13 Paper Mills (2621)

Ten of the 17 Maine PCS pulp and paper facilities have *Average Limits* for mercury effluent concentrations (ME DEP, 2001). The Average Limits are the 95th percentile probability limit on the mean, based on a required number of samples and using EPA methods 1669 and 1631 (ultra-clean techniques) for collection and analysis of samples, respectively. The average of the Average Limit values is 13.0 ppt (ng/L). With a range of 4.5 ppt to 28.9 ppt, where 4.5 is the minimum set by the regulation rather than that measurements. The difference in Average Limits by SIC is not large at 14.4 ppt for pulp mills and 12.4 ppt for paper mills. Of the 10, only three had flow rate values in PCS: 34.0, 46.5, and 157 MGD, for an average of 79.2 MGD.

In order to compare the PCS loads with loads based on average effluent concentration, a conversion from effluent concentration in ppt (or ng/L) times flow rate in MGD to lbs/yr is required, as follows.
10-9 g/ng x 1kg/10^3 g x 2.2046 lb/kg x 3.785 L/gal x 10^6 gal/MG x 365 D/yr
= 0.003046 lb/yr /(MGD - ng/L)
So the Average Limit for Pulp and Paper Mills is converted as follows
13.0 ng/L x 79.2 MGD x 0.003046 lb/yr/ (MGD - ng/L) = 3.14 lb/yr
So, an estimated mercury loading rate value of 3.1 lb/yr will be applied to each pulp and paper mill in PCS.

Publicly Owned Treatment Works (POTWs):
From the PCS data coverage, a query for SIC = 4952 resulted in a coverage of 23,629 POTW facilities in the conterminous U.S. For each watershed, then, the sum of the flows from POTWs were summed, and multiplied by a mean effluent mercury concentration to get an estimated direct waterbody discharge load estimate (in lbs/yr) (see Pulp and Paper Mills section for conversion factor). A study by the Association of Metropolitan Sewerage Agencies (AMSA) found an average concentration of 7 ppt in wastewater treatment plant effluent (Nellor, 1999). This data is based on AMSA's study of 24 POTW facilities in six states, using clean sampling and analytical techniques, for facilities with a range of flow rates from 0.65 MGD to 225 MGD, serving populations ranging from 18,2000 to 1.74 million (median population - 384,000).

Applying this average concentration to the reported flow rate of each facility resulted in a mean watershed load of 0.69 lbs/yr, with a range from 0.0 to 128 lbs/yr, and a total load of 472 lbs/yr, for the 681 watersheds with POTWs. Based on this screening analysis, 79 watersheds had total estimated POTW mercury discharge loads greater than 5% of an estimated typical air deposition load delivered to waterbodies (i.e. 20% of a "typical" 10 ug/m^2/yr deposition rate) or 1% of the typical air deposition rate times the watershed area. All watersheds screened out by this approach are located west of the Mississippi River. In these 79 watersheds, POTW effluent may constitute a significant source of mercury to receiving waterbodies and thus these watersheds will be eliminated from the analysis.

For comparison purposes, the data on POTW mercury loads in PCS are discussed below. Of all POTW facilities, 1946 have PCS mercury loading data with a range of average annual loads (all facilities per year) from 34 lbs/yr to 1,200,000 lbs/yr, with a maximum reported value of 1,000,000,000 lbs/yr from a facility in GA. Of all reported mercury loading values (not summarized by year or facility), 99% are 1000 lbs/yr or less, while 37% are zero. While there has been a steady increase in the number of facilities reporting mercury loads, from 1990 to 1999, loading does not appear to have a specific pattern with respect to time. While one would expect average loading rates to go down, as new mercury analytical and clean sampling techniques came into use in the late 90's, data from 1997 and 1998 have the highest average loading for the entire ten year period. In sum, mercury loading data in the PCS database has

some obviously suspect figures, as well as generally having reported loading rate values much higher than values reported in the AMSA study.

Mercury Cell Chlor-Alkali Production Facilities:

The PCS theme was queried for the 14 mercury cell chlor-alkali facilities listed in the Mercury Study Report to Congress (MSRC, 1997), and developed into a separate theme. The mercury cell chlor-alkali facilities theme was linked to the PCS mercury loading data table.

Joining the mercury cell chlor-alkali theme with the PCS mercury loading data shows an average annual load of 39.7 lb/yr, with a minimum of 0.0 lb/yr and a maximum of 1659 lb/yr (one year maximum, Occidental, Muscle Shoals, AL). The next highest value at that plant was 53.0 lb/yr and the next highest at any other plant was 152 lb/yr.

While the PCS data is generally thought to be unreliable due to the use of non-ultra-clean sampling and analytical techniques, no other data source, sufficient to derive a reliable screening level estimate, was found. Evidence of faulty data in PCS can be found by comparing reported loading rate data for the Olin Corp facility in Augusta, GA. Reported at 32.5 lb/yr mercury effluent load in PCS, this same facility was sampled recently, as part of the Savannah River mercury TMDL and estimated to discharge 0.95 lb/yr (EPA, 2001).

Mercury Maps
A Quantitative Spatial Link Between Air Deposition and Fish Tissue

Internal Peer Review
Response to Comments

Paul Cocca
Standards and Health Protection Division
Office of Science and Technology
Office of Water
8/17/01

1a) Is the reduced-form model, presented in this report, an accurate characterization of the air deposition load / fish tissue concentration relationship, predicted by the IEM-2M and MCM models at steady state?

Comments:
Two reviewers declined to comment, stating it was out of their area of expertise.

1a-1) One reviewer, familiar with the two models, stated that the models are in fact linear at steady state.

1a-2) Another reviewer stated that the models are similar at steady state, though there would need to be validation and verification to confirm they are equivalent. The reviewer suggested, in particular, looking at the sensitivity of the two models (i.e. Mercury Maps model versus IEM-2M and MCM), and how they react to perturbations to same model components.

Response:
1a-1) The acceptance of the reduced-form model, by the one reviewer, is of substantial weight, as this reviewer has significant experience with the IEM-2M and MCM models from their work on the Mercury Study Report to Congress (MSRC) (EPA, 1997).

1a-2) In response to the other comment, the application of the E-MCM model in the Everglades Pilot Mercury TMDL (USEPA, 2000), is compared below with what Mercury Maps would predict for the same site.

The Everglades Pilot Project Mercury TMDL (USEPA, 2000), determined the relationship between atmospheric Hg(II) deposition and long-term fish tissue mercury concentrations, in Everglades Site WCA 3A-15. To determine the relationship, the researchers first calibrated the E-MCM to the WCA 3A-15 site and ran the model for 100 years to achieve an approximate steady state response to the current air deposition loading rate. They compared these long-term predicted results against current measured water, sediment, and fish concentrations and found an acceptable match. They then reduced the mercury deposition load, as well as watershed mercury inflows, and ran the model for an additional 100 years; performing this process separately for 25%, 50%, 75%, and 85% reductions in overall loads. In plotting the results of the above analysis, the researchers found the relationship between fish mercury concentration and mercury air deposition rate to be linear, and to fit the equation: $Y = 0.9408X + 0.0611$, where Y = the fraction of current fish concentration; and X = fraction of current air deposition load (wet and dry). By comparison, the Mercury Maps model simply states $Y = X$ (i.e. slope =1, and intercept = 0). The reasons for the discrepancy between the two models, as well as the effect on predictive accuracy of the Mercury Maps model, are discussed below.

The researchers note the reason for the slope and intercept, of the fitted equation, not being equal to one and zero, respectively, is that even after the initial 100 year simulation, deep sediment concentrations had not yet reached a steady state response to current loading. The sediment concentrations are elevated with respect to true steady state, and thus represent an additional load beyond the reduced air deposition load. The researchers also state that were the simulations carried out for much longer periods (as long as thousands of years), predicted concentrations would approach a direct proportional response (i.e. Y = X).

The E-MCM model result, being not quite directly proportional, can be shown to have a quantifiable effect on the predictive accuracy of the Mercury Maps model, were it also applied to the Everglades WCA 3A-15 site. For a 50% reduction in air deposition load, the Everglades Hg TMDL application would predict a 47% reduction in fish concentrations, to Mercury Maps' 50% reduction. Higher proportional reductions result in larger prediction errors, e.g. a 90% air deposition load reduction causing a 84% fish tissue reduction in E-MCM, versus a 90% reduction in Mercury Maps.

In conclusion, sediment concentrations may, in some instances like the Everglades WCA 3A-15 site, be elevated with respect to current air deposition loads. These elevated concentrations, unaccounted for in Mercury Maps, act as an additional source and, where significant, will cause Mercury Maps to over-predict reductions in fish tissue concentrations. In the case of the Everglades site WCA 3A-15, the quantified over-prediction is relatively small, on the order of up to five percent at high air deposition rate reductions. In addition, it can be reasonably expected that similar situations exist in other watersheds throughout the U.S., where historic atmospheric mercury deposition and continued mercury accumulation in sediments may cause current sediment concentrations to be elevated with respect to current deposition levels, but that these elevated levels will cause fish concentrations to depart only slightly from the direct proportional reduction used in Mercury Maps. This small difference is likely reasonable for the purposes of benefits assessments.

In addition to the Everglades pilot mercury TMDL study, a TMDL was performed and finalized for the Savannah River using models that are similar to IEM-2M and MCM. In the *TMDL Determination* section of this report (USEPA, 2001), the authors state that "Because the water column mercury concentration response is linear with respect to changes in load, a proportion can be developed to calculate the total maximum mercury load from the watershed that would achieve the derived water quality standard ..." The TMDL was determined by taking the ratio of the existing stream concentrations to the water quality standard, and equating that to ratio of the current load to the TMDL load. And, in relating the TMDL stream load back to atmospheric reductions (atmospheric sources accounted for 99% of the total load), no differentiation was made between the percent reduction in atmospheric load to the watershed and the percent reduction in atmospheric load delivered to the waterbody, implying a linear relationship.

1b) Is it accurate to say that in watersheds where the mercury load to water bodies is dominated by air deposition, mercury concentrations in fish tissue are expected to reduce in direct proportion to reductions in mercury deposition, at steady state?

Comments:
This question received the most discussion from the reviewers.
1b-1) A key issue raised by two of four reviewers is that other sources, if present in significant quantities, would cause the relationship to be *non-linear*, and/or to not go through the origin (i.e. fractional fish tissue concentration reductions would be of the form: a + b*[%_air_reduction]). One reviewer pointed out that not taking into account background sources constitutes a negative margin of safety. That is, the proportional reduction method would predict larger reductions than would actually occur, were other sources to be of sufficient magnitude. Potential *other* sources listed by the reviewers included:
1b-1A) Weathering and dissolution of mercury from bedrock;
1b-1B) Vegetative capture of inert atmospheric elemental mercury; the reviewer states that current air deposition models do not take this into account, and that elemental mercury is the form of mercury that will contain the highest fraction of *background* mercury (i.e. from natural and international sources) thus making this a potentially large source; and
1b-1C) Non air deposition sources identified in the project as potentially significant (e.g. mercury and gold mines, and mercury cell chlor-alkali facilities); the reviewer stated that including a more sophisticated equation/model would allow these watersheds to be included in the analysis.

1b-2) A third reviewer pointed to a recent study, published in ES&T that found an increased demethylation rate in areas of high environmental mercury levels. That is, net methylation may be lower in areas of high mercury concentrations, and thus fish tissue levels would be higher that expected under a proportional decrease.

1b-3) Finally, a fourth reviewer pointed out that what might seem to be steady state conditions, found while monitoring, could be upset by a number of extreme environmental/meteorological events causing the release of mercury *locked-up* in the watershed, having been set there by historical deposition. For example, extreme high river flows could cause resuspension of deep riverine sediments containing elevated mercury concentrations. Another example is re-inundation of the littoral zone during the return to normal water levels following an extended drought, releasing mercury bound up in vegetation and soils as it's re-exposed to a methylating environment.

Response:
It's important to distinguish between the two different types of *non-linear* responses mentioned by reviewers. In one case, discussed in response 1b-1, other sources cause the plot of fish tissue concentrations versus air deposition rates to not go through the origin, thus causing a simple proportional reduction to over predict actual reductions in fish tissue concentration. In another

case, discussed in response 1b-2, non-linear reaction rate kinetics cause biochemical processes to alter methylmercury concentrations in the environment in a manner which is not linear with respect to total load. Finally, as discussed in 1b-3, time to steady state may be exceedingly long, or appear to have been achieved, only to be upset by the release of environmentally sequestered mercury.

1b-1) In cases where air deposition is not the sole significant source, as in the Everglades example cited previously, the equation describing fish tissue fractional reduction would need to be modified as follows, as per the suggestion of the reviewer:

Eqn. 1.
$$\frac{C_{fish_2}}{C_{fish_1}} = \frac{\left(L_{Air_2} + L_{Other}\right)}{\left(L_{Air_1} + L_{Other}\right)}$$

Where:

C_{fish2} = concentration of mercury in fish at time 2
C_{fish1} = concentration of mercury in fish at time 1
L_{Air2} = air deposition mercury load to waterbody at time 2
L_{Air1} = air deposition mercury load to waterbody at time 1
L_{Other} = non air deposition load of mercury to waterbody

and which reduces to the simple proportional reduction, when $L_{Other} = 0$.

For the above equation, it can be shown that:

Eqn 2.
$$\frac{C_{fish_2}}{C_{fish1}} = \frac{L_{Air_1}}{\left(L_{Air_1} + L_{Other}\right)} \cdot \frac{L_{Air_2}}{L_{Air_1}} + \frac{L_{Other}}{\left(L_{Air_1} + L_{Other}\right)}$$

which is of the form Y = mX + b
where:

Y = fractional reduction in fish tissue concentration;
X = fractional reduction in air deposition load;
m = slope; and
b = y-intercept.

It can be shown that, for equation 2, m + b = 1. As well, the intercept (b) is just the *other load* as a fraction of total load. In the case of the Everglades mercury TMDL Pilot Project, m = 0.94, while b = 0.06. That is, 6% of the total load is non-air-deposition load.

The method employed in this project, then is to eliminate from the analysis those watersheds where sources other than air deposition are significant, thus keeping b close to zero, and m close to one, reducing errors in using the direct proportion methodology (i.e. Y = X). Below, is the

response to the possibility raised by comments 1b-1A and 1b-1B that there may be potential sources not taken into account by this project, as well as, in response to comment 1b-1C, further explanation of the reasoning behind eliminating known or likely significant point sources from the analysis. Based on the studies summarized briefly in response 1b-1A, below, it appears unlikely that background sources contribute a significant fraction of the current load. Also, as discussed in response 1a-2, the error likely to have been introduced, by not taking into account the effect of background load on predicted response, is small relative to the prediction. Finally, this error may serve to offset the under-prediction of benefits discussed below in 1b-1C.

1b-1A) A number of studies have looked at the potential relationship between mercury concentrations in soil and runoff, as well as soil/bedrock erosion as a potential mercury source. St. Louis, et al, 1996 estimated, based on comparisons with erosion rates of other minerals, that mercury weathering rates could range from 0.4% to 6% of total mercury inputs to the watershed. They deemed this amount insignificant for the purposes of the mass balance in their study. Finally, Aastrup, et al, 1991 quantified mercury accumulation and transport in a number of soil layers in a watershed, as fractions of total mercury deposited. By the use of a mass balance they demonstrated that the content and fluxes of mercury, in interflow and groundwater flow, is accounted for via the percolation of atmospherically deposited mercury through the soil. In addition, while weathering and dissolution of mercury from bedrock may be significant in some areas, these areas would likely be associated with mercury mining locations, and would be screened from the analysis on that basis.

1b-1B) The scenario described by the commenter, is one in which a deposition pathway (in this case, vegetative capture of inert atmospheric elemental mercury, reflective of impacts from background atmospheric mercury levels), is not taken into account. As deposition from local and regional sources diminishes, in response to source controls, the relative contribution from background would become greater. As described above in equations 1 and 2, if this deposition pathway were not taken into account, it would act as an unaccounted for source, causing Mercury Maps to over-predict an expected reduction in mercury concentrations in fish tissue. While this scenario is plausible, there are several reasons why it's not directly relevant to the Mercury Maps project.

In the case of adsorption of elemental mercury by vegetation, the air deposition model REMSAD does take into account vegetative properties in estimating dry deposition. The deposition velocity is the inverse sum (resistances in series) of aerodynamic, boundary layer, and surface resistances. Stomatal resistance is included as a component in surface resistances (SAI, 1996). It should be noted that REMSAD does not take into account the reverse and balancing process of volatilization of mercury from either the land surface or vegetation. Since this would tend to increase net flux of elemental mercury to watershed surfaces, it would appear that REMSAD may in fact over-predict the impact of background elemental mercury levels thus diminishing the impact of emission controls on deposition rate and thus fish concentration.

In addition, while the accuracy of predictions of fish tissue reductions in Mercury Maps will be a direct reflection of the accuracy of the air deposition model in predicting relative rates of air deposition of mercury to watersheds, this project is not dependent on the use of any particular deposition model. Rather, this project is intended to be coupled with the air deposition model thought best able to predict percent reductions in mercury deposition on a national scale.

Finally, it should be noted that any potential for non-linearity in the selected air deposition model should not be confused with the potential for non-linearity in watershed fate and transport. The air deposition model need not be linear with respect to source loadings to the atmosphere in order to be used in conjunction with Mercury Maps.

1b-1C) The approach suggested by the reviewer is outlined in response 1b-1, discussed above. Based on additional analyses of point source data, discussed in section 2c-NA and the Appendix, a new approach of eliminating watersheds where the expected sum of loads from pulp and paper mills and POTWs exceeds 5% of expected waterbody-delivered air deposition loads, as well as eliminating watersheds with mercury mines, significant gold mines, and/or chlor-alkali facilities, is used. While the commenter's model, presented above, would allow other significant sources, to be included in the analysis, the quality in the data characterizing loads from these sources is insufficient for use in other than a screening level approach. Loads from POTWs and pulp and paper mills are simply estimates based on the product of facility flow rates and average measured mercury effluent concentrations. There was insufficient data to use a similar screening level approach for mercury cell chlor-alkali facilities and estimating loads from abandoned mines would likely require numerous high quality samples. This lack of data quality was a key determinant in selecting an approach that included screening out watersheds with significant or potentially significant non-air-deposition sources. While a national statistical sampling of all permitted discharge facilities, by industry, would provide an adequate base of information to improve on this approach, no such comprehensive data set as of yet exists. In addition, it would be extremely difficult and resource intensive to attain a sufficiently precise nationwide data set on mercury loads from other nonpoint sources such as abandoned mines and bedrock erosion.

It should be noted, however, that for the use of Mercury Maps in an emission reduction benefits analysis, the effect of using the watershed elimination method is to under-predict the overall benefits. The extent of this under-prediction can be bounded on the upper end as the percentage of all watersheds that are eliminated (i.e. if 20% of all watersheds are eliminated, the under prediction is, at a maximum, 20%). It should also be noted that this expected under-prediction should be within the realm of uncertainty brought in by other aspects of a benefits assessment. This approach buys a higher degree of certainty at the expense of a potentially higher benefits calculation.

1b-2) The ES&T article (DiPasquale, et al, 2000) found that demethylation rates increased with increased methylmercury concentration, in waterbodies with extreme mercury contamination, caused by historic mining practices. In addition, the researchers found that demethylation

decreased over time as methylmercury concentrations in samples decreased, for all three test areas, including the Everglades. While this study does appear to provide real evidence of a nonlinear process with respect to mercury concentration, it is not clear whether net methylmercury bioaccumulation in fish is expected to be a nonlinear function of mercury concentration as a result. Potentially, additional nonlinear processes could serve to cancel out the nonlinearity in demethylation, resulting in a linear net bioaccumulation function. Finally, the correlation of higher degradation rates with higher contaminant levels does not necessarily connote a causality. There may be independent factors causing both.

However, were nonlinear demethylation rates to affect net bioaccumulation in this way (i.e. to cause fish tissue concentration reductions to slow with decreased load) the proportional reduction approach in Mercury Maps would then overpredict reductions in fish tissue. That is, the potential implication of DiPasquale, et al, 2000 is that more dramatic deposition reductions, than those derived in the current formulation of Mercury Maps, would be required in order to achieve the methylmercury criterion in all watersheds. Conversely, for a given technological standard based emission reduction, the estimated benefits would be reduced.

1b-3) While extreme events may unlock mercury from environmental pools, this is part of an expected uneven response over time to reduced mercury loadings to watersheds and waterbodies. Also referred to as dynamic equilibrium, steady state in environmental systems means that concentrations may vary season to season or even year to year, but that long term averages are constant. While environmental media mercury concentrations are expected to trend downward, random fluctuations in meteorological and other environmental patterns will cause uneven responses. The Everglades Mercury Pilot Project TMDL (discussed above in response to 1a-2) is a good demonstration of how mercury from historic deposition, can remain in the sediments for long periods of time before achieving true steady state.

2a) Can the fish tissue data be used for the purposes outlined, given its origins, quality, and completeness?

Comments:
2a-1) Reviewers pointed out that the average fish concentration across a watershed is not necessarily representative of the population of fish eaten, nor of the true average for their watershed. Reviewers mentioned a number of potential separate causes:
2a-1A) States might sample predominantly for sport fish (i.e. trophic level four fish), though people likely consume a wider variety of fish including those in trophic level three;
2a-1B) The fish sampled may not be truly representative of the true population average across the HUC;
2a-1C) Some fish consumers may favor fish from a particular waterbody, i.e. one that is a local maxima, and thus could be unduly exposed to a higher than acceptable body burden.

2a-2) In addition, one reviewer pointed out that different sampling procedures (selection of site and fish species) in different jurisdictions could distort the regional picture.

2a-3) Finally, another reviewer pointed out that not all samples will be of the same type (i.e. fillets versus whole fish versus composites) and stated that they should be uniform across the analysis.

Response:
2a-1) It is true that the fish sampled are not necessarily representative of the population of fish actually consumed, which could potentially introduce certain biases in the analysis. The stated purpose of this product is to establish a method of quantitatively predicting the spatial distribution and extent of reductions in fish tissue mercury concentrations, in response to a given spatially distributed reduction in air-deposited mercury watershed loads. Simply stated, then, Mercury Maps will predict concentration reductions for those fish tissue data used. The commenter's suggestions are most relevant to inform the intended use of Mercury Maps, particularly for the intended uses: assessment of benefits of reduced mercury emissions. The responses below are intended to show how biases and potential biases in the fish tissue data used, may influence the use of Mercury Maps in benefits assessment. It should be noted, there are two entirely different approaches to performing a benefits assessment for reductions in fish tissue mercury concentrations: 1. Estimate reductions in fish advisories and thus reduced economic impact; or 2. Estimate reduced health impact from reduced fish tissue contaminant concentrations. In addition, another potential use of Mercury Maps is in performing a regional or national TMDL analysis, and/or in developing a risk-based mercury emission reduction rule. In both cases, local maxima in fish tissue mercury concentrations are of primary concern.

2a-1A) The fish tissue database is apparently biased towards trophic level 4 fish (typically sport fish). Looking at the top ten most frequent species of georeferenced samples, 12,422 (83%) are trophic level 4 (largemouth bass, walleye, northern pike, channel catfish, yellow perch, and smallmouth bass, in descending order of frequency), while 2608 (17%) are trophic level 3 (common carp, bluegill sunfish, white sucker, and black crappie, again in descending order of frequency). One of the intended uses of the Mercury Maps project is as a component in a quantitative benefits analysis for national technology-based air emission reduction rules. For use in such a benefits analysis, the Relative Source Contribution (RSC) approach suggested by the reviewer would appear unnecessary, since the percent reduction in concentration is expected to be the same, regardless of species, trophic level, or average concentration. However, were the benefits analysis to take into account changes in diet (e.g. as a result of lifting of fish consumption advisories), use of a RSC approach would be reasonable, given the clear bias in fish sampling.

2a-1B) Since these data are used by States in making decisions on whether to post fishing advisories, the fish sampled may not be truly representative of the true population average across the HUC. These samples are in fact generally based on areas that are most heavily fished (*angling pressure*) and/or those that are suspected of having higher than average potential to be

polluted (AFS, 2000). That is, the average concentration may be biased higher with respect to the true average, but would be expected to be more reflective of the average concentrations in consumed freshwater fish. While a statistical sampling would produce a less biased average concentration, the goal of protecting human health is better served by sampling with a bias towards areas, that with sound scientific reasons, are suspected of having higher than average concentrations, or that account for a disproportionate amount of fish caught and consumed. The manner in which fish tissue is sampled is a decision made by the state agency. Additional analyses on the fish tissue data are included in the Appendix. It should be noted that the median number of samples per HUC is 9 (mean is 24), which is a reasonable statistical sample on which to base a mean.

2a-1C) The reviewer notes that were a waterbody, with fish tissue concentrations elevated with respect to the HUC-wide average (i.e. a local maxima), to be the primary source of fish for a particular consumer group, these consumers could be unduly exposed to a higher than acceptable body burden. While an average HUC-wide concentration is not representative of any particular waterbody within the watershed, the few samples taken from any particular waterbody are less likely to be representative of the average concentrations in that particular waterbody. This aggregation of the data is appropriate given the density of the coverage. That is, at a median number of samples per HUC of 9 (see Appendix), the mean can be expected to reasonably represent the watershed average much better than one to a few samples represent a waterbody average.

2a-2) As discussed in 2a-1b, the average concentration may be biased higher with respect to the true average, but would be expected to be biased towards areas that are most heavily fished and/or those that are suspected of having higher than average mercury concentrations. In that way the sampling site selection procedures are likely similar. On the other hand, due to differences in species abundance, fishing preferences, and consumption preferences, one would expect States to adopt sampling practices that were different from their neighbors, but most appropriate for their fishing citizenry. For this reason, data collected for a single purpose, would be a much better measure of the *actual* distribution of mercury in fish throughout the country. But for the purposes of evaluating the benefits of reduced mercury concentrations in fish, particularly regarding the elimination of fish consumption advisories, the expected biases of the data may actually improve its utility.

2a-3) In response to the commenters note that all samples were likely not of the same type and that the data should be filtered to a single type for this analysis, a statistical analysis of the different types was performed. It was found that there were large differences between fillet and whole fish concentrations (0.40 ppm vs. 0.18 ppm, respectively), as well as between fillets with skin off versus fillets with skin on (0.40 ppm vs. 0.31 ppm, respectively). It was also shown that these differences in concentrations may be due in large part to differences in species sampled. Whole fish samples are more frequently trophic level 3 fish, while having skin on or off appears to be a function of how a particular fish species is typically consumed (see Appendix for details). Based on this analysis, and because for the purposes of benefits assessment, TMDLs, and risk-

based emission control rules, the consumed concentration is most relevant, whole fish samples are eliminated from the analysis, and all fillets (skin on and skin off) are included. All unknown and unspecified sample types are eliminated from the analysis.

2a-NA) Since the September, 2000 cut, the Fish Advisory fish tissue database was updated. An additional 1,400 samples were added to the database since that time. These additional records were added to Mercury Maps fish data, making it current as of June, 2001.

2b) Is the scale of the analysis appropriate?

Comments:
Two reviewers did not address this question.
The response of the remaining two reviewers, toward the HUC8 scale of analysis, however, was positive with one reviewer stating that "the scale of the analysis gives a good picture of where reductions in mercury deposition are needed" and another pointing out that the USGS is using a similar scale in their analysis. However, one reviewer did point out that a watershed-wide average may mask local minima and thus not be protective of consumers who get their fish from a single water body or subwatershed area with higher than average concentrations. Another reviewer pointed out that the USGS is moving toward a finer resolution analysis, such that they can evaluate issues of scale by aggregating data at different scales, thus addressing the issue of scale up front by performing the analysis at the finest resolution and addressing the issues of scale simply by viewing the results of different levels of aggregation.

Response:
A preliminary analysis of the effect of using a finer resolution watershed coverage was performed. The HUC-11 watershed coverage, readily available for the Chesapeake Bay watershed, was added to the project, and fish tissue data were aggregated to that level of resolution. The resulting map of the average fish tissue concentration relative to the methylmercury criterion showed a few local maxima that had been smoothed out at the higher resolution HUC8 watershed scale, as is to be expected. An analysis, presented in the Appendix (fish tissue database section), however, shows that the median number of samples in the HUC11 watersheds is 3, while the median in HUC8 watersheds is 9. That is, while the fish tissue database is substantial, it is not large enough to justify averaging across watersheds smaller than the HUC8 level. This effect was also discussed in response 2a-1C, with respect to waterbody specific analyses. Analyses at smaller levels is justified on a case by case basis, and may be appropriate in a sentinel-watershed approach associated with a risk-based air emission reduction rule analysis, or a TMDL.

2c) Is the use of all other data layers in addressing the goals of the project, appropriate, taking into account their origins as well as their quality and completeness?

Comments:

Two reviewers did not address this question other than to say that data quality and completeness are important and should be taken into account.

2c-1) One reviewer pointed out that the screening of watersheds for NPDES permitted mercury discharges, took 5% of the deposition load to the watershed, but that it should rather take 5% of the air deposition load delivered to waterbodies. The reviewer stated that the percent delivered is on the order of 1-10% of the total deposition.

2c-2) Another reviewer suggested taking into account pulp and paper mills, that though they are not likely significant mercury dischargers now, they may have been earlier, and thus affected fish tissue samples from 1990 to 1995.

Response:

2c-1) The reviewer correctly pointed out that pollutant discharge loads to waterbodies were being compared directly with air deposition loads to watersheds. The following is a review of the literature on the percent of total atmospheric deposited mercury which is transported from watersheds to receiving waterbodies.

- Aastrup, et al, 1991 found yearly mercury transport to a lake from a forested subcatchment to be 17% of total mercury deposition.
- Lindberg, 1996 found the combination of runoff and leaching to total 3.5% of total atmospheric load of mercury to the Walker Branch watershed, TN.
- St. Louis, et al, 1996 found that for five catchments in the Experimental Lakes Area (ELA) in northwestern Ontario, export of total mercury ranged from an average of 29.5% for a basin wetland to 61.1% for a riverine wetland.
- Sherbatskoy, et al, 1998 found an export rate of 6% of total mercury from a small forested catchment in Vermont.
- Swain, et al, 1992 found for catchments to seven headwater lakes in Minnesota and Wisconsin, the proportion of atmospheric mercury transported from catchment to lake to be 26% and 22% for modern and pre-industrial times, respectively.
- Hurley, et al, 1995, found watershed total mercury transfer efficiencies, for 39 river sites in Wisconsin to range from Fall means of 0.5% to 8% (depending on watershed type) to Spring means of 29% to 90%.
- Tsiros and Ambrose, 1999 found delivery of mercury to canals in the Everglades Agricultural Area was 23% of atmospheric deposition.
- Johansson et al. (1991) reported mercury transport fluxes from several small watersheds to be about 30% of atmospheric deposition.
- Tsiros, 2001, in model simulations, found that mercury runoff flux was 2 to 3 times higher than normal during wet years, and 5 to 7 times lower than normal during dry years, and that mercury runoff flux was 18% to 61% of atmospheric deposition for wet years, and 1% to 4% of deposition for dry years. These values correspond to runoff flux for normal years to be between 6% and 30% of deposition.

Based on a review of the above studies, it appears that a delivery ratio of 20% is a reasonable estimate of the central tendency of this value, an appropriate estimate for the purposes of this study. That is to say, on average, it's expected that only 20% of air deposited mercury reaches

waterbodies on a long-term average annual rate. Rather than comparing water discharge loads to 5% of air deposition, then, they will be compared to 20% of 5% or 1% of the *typical* air deposition rate.

2c-2) In response to this comment, pulp and paper mills were also considered as potentially significant sources. In addition, due to known uncertainties in PCS data for mercury, a new methodology for screening out sources was developed. A detailed review of a study conducted by the Maine DEP (ME DEP, 2001) found 3.1 lb/yr to be the expected loading rate for both pulp mills and paper mills. That is, the 14 pulp and paper mills in the study had an average concentration of 13 ppt, and an average flow rate of 79 MGD (see Appendix for details). By contrast, PCS data showed average loading data of 10 lb/yr for pulp mills and 40 lb/yr for paper mills (see Appendix). As the PCS data is likely based on a non-ultra-clean techniques it will not be used. While of the 14 current chlor-alkali facilities, only one is classified as a pulp or paper mill, pulp and paper mills more commonly used in-house mercury cell chlorine production facilities in the past. Past mercury sampling and analytical techniques, in which the use of non-ultra-clean techniques resulted in sample contamination, and falsely high results may also have influenced the perception of pulp and paper mills as significant mercury dischargers. The mid-90's date is the time in which ultra-clean sampling techniques were becoming recognized as producing more accurate mercury water column concentration data.

2c-NA) In addition, though not discussed by the reviewers, additional data analyses were performed in order to address data quality issues identified in the PCS data. The watershed screening methodology was improved by using additional data sources for POTWs, chlor-alkali facilities, and gold mines.

Publicly Owned Treatment Works (POTWs):
Using a study conducted by the Association of Metropolitan Sewerage Agencies (AMSA) on mercury in POTW effluent, a sensitivity analysis was performed to examine the relative loading from POTWs versus air deposition delivered to waterbodies. Nellor, 1999 cites an average mercury concentration in POTW effluents of 7.25 ppt (ng/L). This data is based on AMSA's study of 24 POTW facilities in six states, using clean sampling and analytical techniques, for facilities with a range of flow rates from 0.65 MGD to 225 MGD. The range in mercury effluent concentrations was 0.7 ppt to 69.9 ppt, with a median value of 5.0 ppt.

For the purposes of this study, the mean value of 7 ng/L was applied to each POTW, at the PCS reported flow rate, and summed their cumulative load (across HUCs). This loading rate is compared to a typical air deposition load of 10 ug/m2/yr, with an assumed 20% delivery to waterbodies. If the sum of POTW mercury loads is greater than 5% of the air deposition load, as delivered to waterbodies, then the watershed is screened from the analysis. 79 watersheds were screened out solely on the basis of this procedure, all located west of the Mississippi River. Additional details on this analysis, as well as on the mercury data available in the PCS database, are available in the Appendix.

Chlor-Alkali Facilities:
The screening Procedure for chlor-alkali facilities was also examined and improved as follows. The Mercury Study Report to Congress (MSRC) (EPA, 1997) notes that only a fraction of chlor-alkali facilities use the mercury cell process. MSRC lists the 14 facilities using the process at that time and notes that no new mercury cell chlor-alkali facilities are planned to be built, while a recent study (EPA, 2001) found a much lower loading rate than reported in PCS (see Appendix for details). However, because, recent data were available for only one mercury cell chlor-alkali plant, there were insufficient data to assign an average value across all plants, in a screening approach, similar to that for pulp and paper mills. Instead, the simple presence of a plant will be used to screen out watersheds.

Gold Mines:
Locations with gold as a commodity in the MAS/MILS database included numerous locations that were likely insignificant sources and may have never used the mercury amalgamation process. An alternate database, the USGS Database of Significant Deposits of Gold, Silver, Copper, Lead, and Zinc in the United States was used instead (Long, et al, 1998). This database was queried for mines that have produced more than two tons of gold. Any watershed containing one or more of these mines was screened from the analysis, on the basis of potential historical contamination of the watershed due to use of the mercury amalgamation process.

Mercury Mines:
Plouffe, et al found elevated mercury concentrations in soils surrounding mercury mines, at distances of up to 20 km to 40 km. Thus, it appears reasonable to suspect mercury mines as likely sources of elevated environmental concentrations of mercury.

3) Can the methods developed in this project be used to quantitatively assess impacts of air deposition reductions on fish tissue in air deposition dominated watersheds?

Comments:
One reviewer simply said “yes, I think so.” Another reviewer did not address this question.

3-1) A third reviewer said this approach cannot be used with certainty due to current air deposition models not taking into account orographic effects, and that the only way to know true deposition rates of mercury is to sample them.

3-2) A fourth reviewer suggested a modification to the proportional reduction equations as shown in section 1b-1. The reviewer stated that this equation should be used instead, and that watersheds with other sources should then not be excluded from the analysis.

Response:
3-1) While it’s true that measured deposition rates would be considered a more accurate estimate of true deposition than a modeled result, air deposition models can be compared to and calibrated

against monitoring data, and have the added advantage of providing a more complete data coverage. As discussed previously, the Mercury Maps technique relies on the accuracy of air deposition model results, and incorrect air deposition predictions will be reflected in fish tissue concentration reduction estimates. However, if the air deposition model inaccuracies are proportional to the total load, taking the ratio of future over current deposition load will cancel out these inaccuracies.

Furthermore, REMSAD, the model most likely to be used for the air deposition input to Mercury Maps, has features that represent orographic effects reasonably well. Orographic effects occur when a parcel of warm air meets a mountainside, and is lifted vertically (orographic lifting), thus cooling and condensing, and losing moisture due to precipitation.

In addition to features of its parent model, UAM-V, the REMSAD aerosol and toxics deposition model (ATDM) includes vertical mass redistribution within convective and stratiform clouds, as well as incorporation of a cloud submodel. REMSAD uses 8 vertical layers with sigma (terrain following) vertical coordinates. The first four layers of the model cover the maximum expected daytime planetary boundary layer (typically up to 3.5 km) (SAI, 1996). Since individual cumulus cells are small (1-10km) relative to REMSAD grid cells (50-100km), cloud effects are parameterized in ATDM. The cloud submodel includes a diagnosis of cloud type, and determination of whether deep convection is possible, and if so the mixing coefficient is calculated, fractional cloud cover in the grid column, and net vertical distribution are determined.

3-2) Taking into account *Other* loads, in other than a screening level manner, is infeasible due to large uncertainties in estimating the absolute magnitude of these sources. A more detailed analysis, of individual watersheds, in these cases, is more appropriate. Screening out of watersheds with significant or potentially significant sources allows one to proceed with much greater certainty and credibility, though with a bias towards underestimating overall reductions. The equation suggested by the reviewer, was used in section 1b-1 to illustrate how excursions from the simple proportional reduction model, caused by the presence of *other* sources, could influence the accuracy of Mercury Map predictions. Given that watersheds in which all potentially significant non-air-deposition sources (e.g. point sources and historic mining activities) are eliminated from the analysis, these prediction errors are expected to be quite small.

4) Were the calculations performed correctly? Were the data processed without error?

Comments: None of the four reviewers addressed this question.

Response: In the revised analysis, I have made the final presentation as clear as possible to a future user. It is recommended that future users check the calculations and datasets used to determine whether all calculations and data processing were performed correctly. In addition to the dataset-specific background information and analysis, information on how each data layer was processed is detailed in each section of the Appendix.

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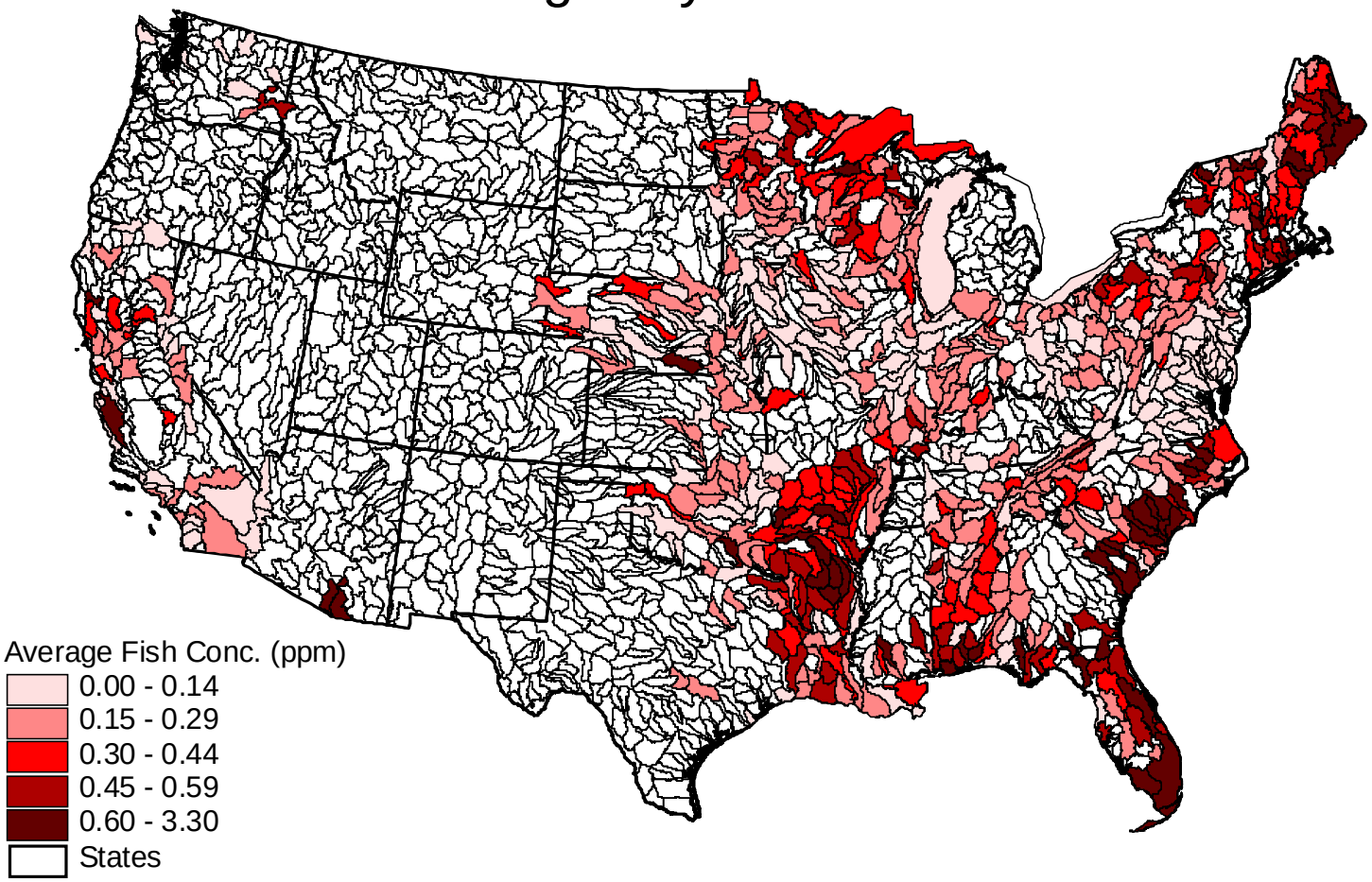
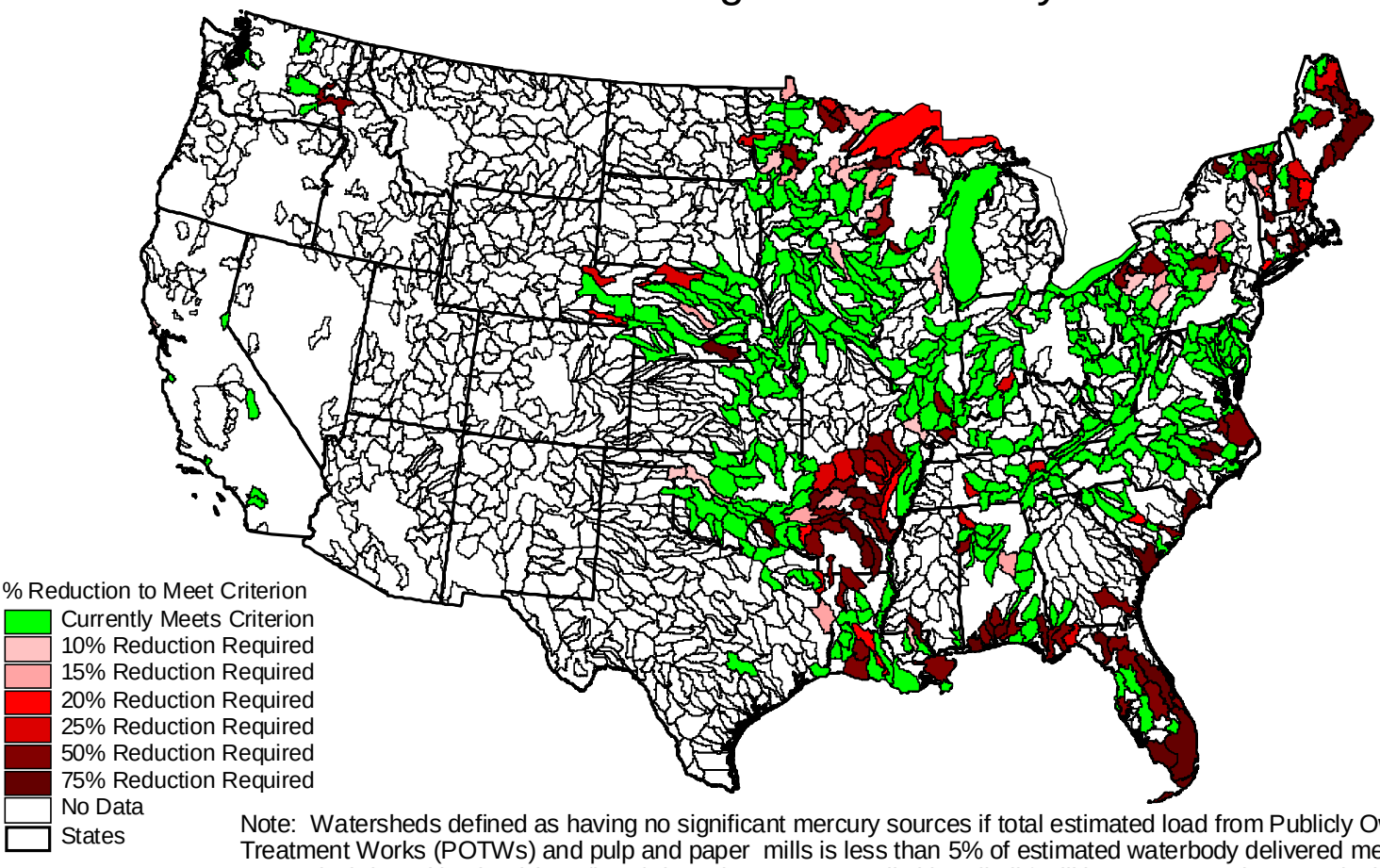
Fish Tissue Mercury Concentrations Averaged by Watershed



Note: New Criterion for mercury in fish is 0.3 ppm. Point of departure in fish advisories often in 0.15 ppm to 0.3 ppm range.
Average value based on fillet samples only. See report text for details.
Source: National Listing of Fish and Wildlife Advisories (NLFWA) Mercury Fish Tissue Database (June, 2001).

Figure 1 (revised)

Percent Reduction in Air Deposition Load Necessary to Meet New Methylmercury Criterion Watersheds with No Other Significant Mercury Sources



Note: Watersheds defined as having no significant mercury sources if total estimated load from Publicly Owned Treatment Works (POTWs) and pulp and paper mills is less than 5% of estimated waterbody delivered mercury at a typical deposition load (10 g/km2/yr), and no mercury cell chlor-alkali facilities, mercury mines, or significant past producer gold mines are present. Additional reductions would be required to meet most state fish advisory levels, which are often set below the methylmercury criterion.
Source: National Listing of Fish and Wildlife Advisories (NLFWA) Mercury Fish Tissue Database (June, 2001). See text of report for data sources for point source dischargers and mines.

Figure 2 (revised)

Additional Data and Analyses for Appendix
(to be merged with report appendix)

Fish Tissue Database

Since methylmercury accumulates in fish muscle, rather than fat, skin, or organs, the manner in which fish samples are analyzed affects the reported concentration. Using whole fish samples will give a reduced concentration, relative to fillets, due to a dilution effect from lower concentrations in non-fillet portions of the fish. While whole fish samples are relevant for concerns over eco-system effects, whole fish sampling is not recommended for use in creating fish consumption advisories (USEPA, 2000b).

Of the 21571 geo-referenced fish tissue samples:

- 17,826 (83%) samples were fillets,
- 1,759 (8%) were whole, and
- 1,986 (9%) were unknown/unspecified.

States in which whole fish sampling composes greater than 25% of all samples, are: GA, IN, KS, MD, ME, NE, and TX. States in which sample type is largely unknown or unspecified are MS (unknown), and TX (year sampled, unknown). About a third of samples in GA are of *unknown* sample type.

Of the fillet samples:

- 3,969 specified with Skin Off,
- 7,570 with Skin On, and
- 5,984 did not specify.

Of all 21,571 samples, only 8 indicated composite sampling, sampled at two separate locations, all done with fillets.

Of the 21,571 geo-referenced samples:

- All fillet shows average concentration of 0.40 ppm;
- All whole shows average concentration of 0.18 ppm;
- Fillet Skin Off shows an average concentration of 0.40 ppm; while
- Fillet Skin On shows average concentration of 0.31 ppm.

In order to assess whether the fish tissue data were biased toward higher trophic level fish, fish tissue samples were sorted by frequency according to species. Of the top five most frequently sampled species of georeferenced whole fish samples, 53% were trophic level 4 fish versus 46% as trophic level 3 fish. Of the five most frequently sampled species of georeferenced fillet samples, 100% were trophic level 4 fish.

Thus, the large difference in concentrations from fillet to whole fish samples is certainly due in part to the different species sampled. However, dilution from using whole fish is still expected to be significant and thus these samples will be removed from the analysis.

The top five most frequently sampled *Fillet Skin On* species were: walleye, northern pike, yellow perch, largemouth bass, and common carp, in that order. While, the top five most frequently sampled *Fillet Skin Off* species were: largemouth bass, channel catfish, white crappie, flathead catfish, and blue catfish, in that order. Based on this listing, it is clear that skin removal is species specific, and likely due to how the fish is commonly consumed. While leaving skin on dilutes the tissue concentration, it appears the choice to remove or retain the skin is representative of how that fish is expected to be consumed, and thus most representative of the concentration consumed. That is, all fillet samples, regardless of whether skin is specified as on, off, or unspecified, will be retained in this analysis.

Sensitivity to Scale (HUC8 versus HUC11) Analysis

The HUC11 watershed coverage was obtained for the Chesapeake Bay drainage. The HUC11 coverage contained 511 HUC11 watersheds compared to 65 in the HUC8 coverage, for the same area, nearly a factor of 8 increase in resolution.

The georeferenced fish tissue data were averaged across the HUC11 watersheds, and compared against the HUC8 coverage. Of the 116 Chesapeake Bay HUC11 watersheds with fish sample data, the median number of samples is 3 (mean of 5), with a range of 1 to 101 (26% have 1 sample). Of the 850 HUC8 watersheds (across the country) with fish tissue data, the median number of samples is 9 (mean of 24), with a range of 1 to 959 (Everglades) samples (11% have 1 sample). While 9 samples should provide a relatively solid statistical measure of the average concentration in the watershed, 3 samples provides a much lower level of statistical significance. At the same time, the dramatic increase in 1 sample watersheds is even more problematic. While the HUC11 watersheds, then, show local maxima exceeding the criterion within HUC8 watersheds shown to be below that level, these high average concentrations are not likely representative.

Database of Significant Deposits of Gold, Silver, Copper, Lead, and Zinc in the U.S.

Source:
This database was obtained directly from the database author, in excel spreadsheet format.

Data Processing:
Fields in the spreadsheet, not needed in the project, were deleted, and the header rows were reduced to a single row with a short, descriptive title. The data was then exported from Excel as a tab-delimited text file, imported to ArcView as a table, added to a View as an Event Theme, converted to a shapefile, and converted to the project projection. The field containing the amount of gold in ounces, previously produced at the mine, was manipulated to remove all non-numeric characters, and converted to number format. This data was queried for mines having produced at least 64,000 ounces (2 tons) of gold. The resultant selection was converted to a shapefile, and imported to Mercury Maps as the gold_mines_sig_dep shapefile.

Notes on Data Quality and Interpretation:
The derivation and quality of data in this database is discussed in considerable detail in Long, et al, 1998.

Permit Compliance System

Pulp and Paper Mills

A separate theme for pulp and paper mills was created from the PCS theme by selecting facilities with SIC = 2611 (Pulp mills), 2621 (Paper mills), or 2631 (Paperboard mills). The PCS database includes 488 pulp and paper mill facilities, distributed as follows:

- 160 Pulp mills
- 244 Paper mills
- 84 Paperboard mills

PCS Loading Data:
The PCS pulp and paper theme was joined with the mercury loading data table, and summarized by year. For each year from 1990 to 1999, between 4 and 14 pulp and paper facilities reported mercury loads. The average load ranged from 5 lbs/year to 228 lbs/year, with the 228 lbs/year value appearing to be an outlier (next highest value is 22 lbs/year and is associated with a facility in Ohio reporting a load of 1324 lbs, and another in NC reporting 261 lbs in 1996). For each of the mill types, the data was summarized by facility (i.e. average load over the ten year period). Of the 27 facilities, average load was 0.0 lbs/year for six of these facilities.

- Pulp mills (SIC = 2611) - average load (by year) ranged from 1.7 to 27 lbs/year, with overall mean of 9.1 lbs/yr.
- Paper mills (SIC = 2621) - average load (by year) ranged from 0.0 to 331 lbs/year, where 7 out of 10 years, average load is less than 5 lbs/year, with overall mean of 35 lbs/year.
- Paperboard mills (SIC = 2631) - average load (by year) ranged from 14 to 261 lbs/year, and overall mean of 44 lbs/year.

Maine Study (1998) Data:
The PCS pulp and paper theme was queried to identify facilities in Maine (NPDES id starting with "ME") and with SIC codes of 2611, 2621, or 2631, resulting in 17 facilities including:

- 4 Pulp Mills (2611)
- 13 Paper Mills (2621)

Ten of the 17 Maine PCS pulp and paper facilities have *Average Limits* for mercury effluent concentrations (ME DEP, 2001). The Average Limits are the 95^{th} percentile probability limit on the mean, based on a required number of samples and using EPA methods 1669 and 1631 (ultra-clean techniques) for collection and analysis of samples, respectively. The average of the Average Limit values is 13.0 ppt (ng/L). With a range of 4.5 ppt to 28.9 ppt, where 4.5 is the minimum set by the regulation rather than that measurements. The difference in Average Limits by SIC is not large at 14.4 ppt for pulp mills and 12.4 ppt for paper mills. Of the 10, only three had flow rate values in PCS: 34.0, 46.5, and 157 MGD, for an average of 79.2 MGD.

In order to compare the PCS loads with loads based on average effluent concentration, a conversion from effluent concentration in ppt (or ng/L) times flow rate in MGD to lbs/yr is required, as follows.
10-9 g/ng x 1kg/10^3 g x 2.2046 lb/kg x 3.785 L/gal x 10^6 gal/MG x 365 D/yr
= 0.003046 lb/yr /(MGD - ng/L)
So the Average Limit for Pulp and Paper Mills is converted as follows
13.0 ng/L x 79.2 MGD x 0.003046 lb/yr/ (MGD - ng/L) = 3.14 lb/yr
So, an estimated mercury loading rate value of 3.1 lb/yr will be applied to each pulp and paper mill in PCS.

Publicly Owned Treatment Works (POTWs)

From the PCS data coverage, a query for SIC = 4952 resulted in a coverage of 23,629 POTW facilities in the conterminous U.S. For each watershed, then, the sum of the flows from POTWs were summed, and multiplied by a mean effluent mercury concentration to get an estimated direct waterbody discharge load estimate (in lbs/yr) (see Pulp and Paper Mills section for conversion factor). A study by the Association of Metropolitan Sewerage Agencies (AMSA) found an average concentration of 7 ppt in wastewater treatment plant effluent (Nellor, 1999). This data is based on AMSA's study of 24 POTW facilities in six states, using clean sampling and analytical techniques, for facilities with a range of flow rates from 0.65 MGD to 225 MGD, serving populations ranging from 18,2000 to 1.74 million (median population - 384,000).

Applying this average concentration to the reported flow rate of each facility resulted in a mean watershed load of 0.69 lbs/yr, with a range from 0.0 to 128 lbs/yr, and a total load of 472 lbs/yr, for the 681 watersheds with POTWs. Based on this screening analysis, 79 watersheds had total estimated POTW mercury discharge loads greater than 5% of an estimated typical air deposition load delivered to waterbodies (i.e. 20% of a "typical" 10 ug/m2/yr deposition rate) or 1% of the typical air deposition rate times the watershed area. All watersheds screened out by this approach are located west of the Mississippi River. In these 79 watersheds, POTW effluent may constitute a significant source of mercury to receiving waterbodies and thus these watersheds will be eliminated from the analysis.

For comparison purposes, the data on POTW mercury loads in PCS are discussed below. Of all POTW facilities, 1946 have PCS mercury loading data with a range of average annual loads (all facilities per year) from 34 lbs/yr to 1,200,000 lbs/yr, with a maximum reported value of 1,000,000,000 lbs/yr from a facility in GA. Of all reported mercury loading values (not summarized by year or facility), 99% are 1000 lbs/yr or less, while 37% are zero. While there has been a steady increase in the number of facilities reporting mercury loads, from 1990 to 1999, loading does not appear to have a specific pattern with respect to time. While one would expect average loading rates to go down, as new mercury analytical and clean sampling techniques came into use in the late 90's, data from 1997 and 1998 have the highest average loading for the entire ten year period. In sum, mercury loading data in the PCS database has

some obviously suspect figures, as well as generally having reported loading rate values much higher than values reported in the AMSA study.

Mercury Cell Chlor-Alkali Production Facilities

The PCS theme was queried for the 14 mercury cell chlor-alkali facilities listed in the Mercury Study Report to Congress (MSRC, 1997), and developed into a separate theme. The mercury cell chlor-alkali facilities theme was linked to the PCS mercury loading data table.

Joining the mercury cell chlor-alkali theme with the PCS mercury loading data shows an average annual load of 39.7 lb/yr, with a minimum of 0.0 lb/yr and a maximum of 1659 lb/yr (one year maximum, Occidental, Muscle Shoals, AL). The next highest value at that plant was 53.0 lb/yr and the next highest at any other plant was 152 lb/yr.

While the PCS data is generally thought to be unreliable due to the use of non-ultra-clean sampling and analytical techniques, no other data source, sufficient to derive a reliable screening level estimate, was found. Evidence of faulty data in PCS can be found by comparing reported loading rate data for the Olin Corp facility in Augusta, GA. Reported at 32.5 lb/yr mercury effluent load in PCS, this same facility was sampled recently, as part of the Savannah River mercury TMDL and estimated to discharge 0.95 lb/yr (EPA, 2001).